and is appreciable only for H_2^+ in vibrational states above the fifth level.[17]

Two points merit further discussion. Mechanism C as written is symbolic of a sequence of excitations in steps, from $v = 0$ to 6, followed by rapid depletion of the populations of states for $v \geq 6$. In such a system, the definition of a "rate constant" is not clear, since T_{vib} cannot be strictly defined. The measured activation energy is only approximately the height of that vibrational level which is filled to *nearly* the Boltzmann population. A complete analysis requires the solution of the coupled equations which express the rates of filling and depleting of the separate levels, say from $v = 0$ to 8, owing to vibrational energy transfer and exchange. Then one need not introduce the "steady-state" approximation. A machine calculation of this model has been started.

The second question pertains to the distribution of the energy of activation (present in the supermolecule) among the reaction products. The postulate that the transition probability is high when the activation energy is localized as vibration in D_2 implies, by microscopic reversibility, that this excess energy will be carried away in the vibrational modes, but probably shared between the DX and HD. Furthermore, when the relative kinetic energy of the reactants is high, it is likely that the relative kinetic energy with which the products leave will also be high, although some redistribution with the vibrational modes will take place.

(17) H. Von Koch and L. Friedman, *J. Chem. Phys.*, **38**, 1115 (1963); T. F. Moran and L. Friedman, *ibid.*, **39**, 2491 (1963); see also A. Weingartshofer and E. M. Clarke, *Phys. Rev. Letters*, **12**, 591 (1964).

Isotope Exchange Rates. II.[1a] Mechanism of the Homogeneous Reaction between Acetylene and Deuterium[1b]

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The homogeneous gas phase reaction between acetylene and deuterium was investigated in a shock tube over the temperature range 1300 to 1665°K. Incident shocks in samples highly diluted with argon (80–87%) were used; compression factors by the shock were in the interval 3.6 to 4.3 for initial total pressures (at 300°K.) of 23–110 mm. The rate of substitution of D for H was followed by recording the emission intensity in the infrared due to C_2HD (at 2555 cm.$^{-1}$) and to C_2H_2 (at 3195 cm.$^{-1}$). The total order for the substitution reaction was 1.24 ± 0.05. It was demonstrated that $d(C_2HD)/dt \cong 2(d(C_2D_2)/dt) \cong -{}^2/{}_3(d(C_2H_2)/dt) = k(D_2)^{1.0} \cdot (C_2H_2)^{0.24}(Ar)^0$. A mechanism consistent with all the data involves two transient species: the complex $C_2H_2 \cdot D_2$, which is readily destroyed by collisions with C_2H_2 molecules, and $C_2H_2D_2{}^*$, which resembles a highly excited ethylene. The effective activation energy for the substitution reaction is 32.5 kcal./mole.

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.

(1) (a) A. Lifshitz, C. Lifshitz, and S. H. Bauer, *J. Am. Chem. Soc.*, **87**, 143 (1965); (b) presented before the Division of Fuel Chemistry, 145th National Meeting of the American Chemical Society, Philadelphia, Pa., 1964.

When one mixes acetylene and hydrogen at these temperatures, no change in the concentration of the acetylene can be detected for as long as 1 msec. 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 following special features of shock tube 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.

The heuristic rate expressions derived from these shock tube data permitted us to establish that the mechanism for H–D substitution in C_2H_2 differs significantly from that in NH_3, H_2S, HCl, and H_2. Further, selection between two plausible transition states

can be made on the basis of the relative amounts of C_2H_2 lost and of C_2HD and C_2D_2 generated.

Experimental

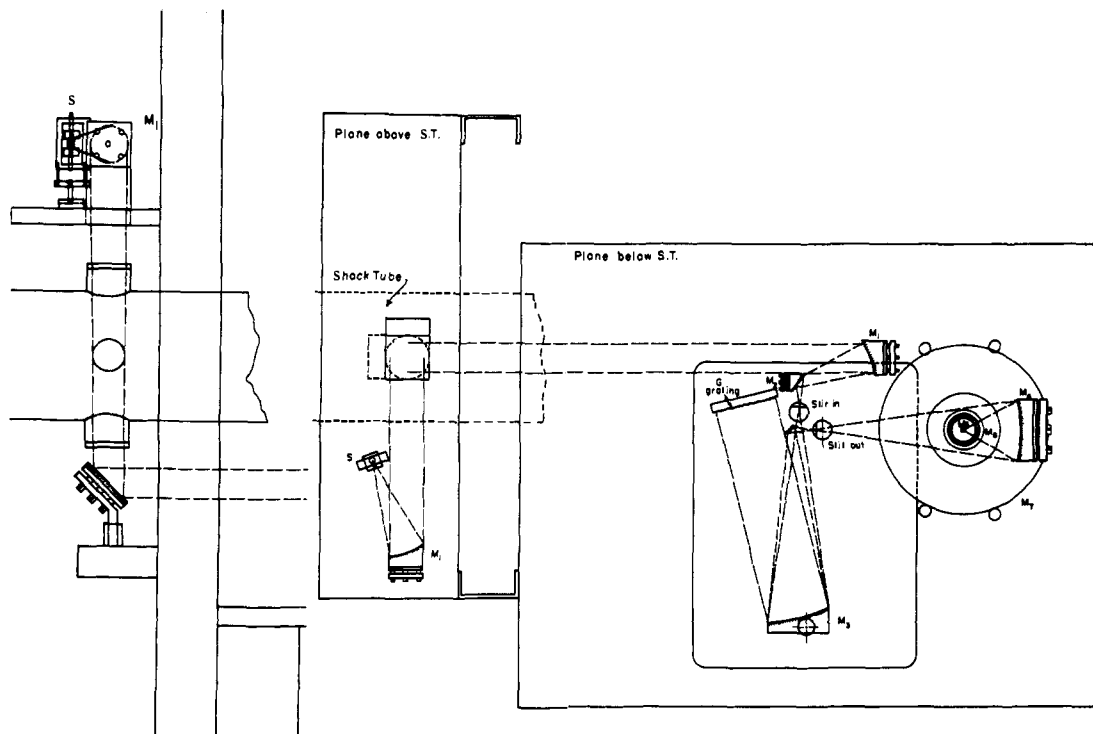*The Shock Tube.* The studies described below were conducted in a stainless steel shock tube, 6 in. in

Figure 1. Partial side view on left and top view of infrared optics: S, Nernst glower (run at 2300 °K.); M_1, 20° off-axis paraboloid (F = 12.7 cm., D = 4.5 cm.); M_2, 35° flat (4.5 × 1.5 cm.); M_1, 14° off-axis paraboloid (F = 26.7 cm.; D = 8.0 cm.); G, grating (B & L No. 33-53-13-88), 83 × 83 mm., 150 lines/mm. (6-μ blaze); M_4, spherical mirror (F = 5.85 cm.; D = 8.0 cm.); M_5, 5 × 5 mm. flat, at 45°; M_6 and M_7, Cassegrain optics.

diameter, for which the driver section was 8 ft. long and the driven section 22 ft. long. Observations were made by recording the infrared emission at selected wave lengths for incident shocks. The windows were located 18 ft. 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 piezoelectric gauge. Mylar diaphragms of 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 (0.5–1.5) × 10^{-4} mm.; the leak rate was less than 1 μ/min. Shocks were run between 2 and 3 min. after filling the tube with premixed gas samples. Hydrogen was used as the driver. Independent tests showed that during our observation time no isotope exchange occurred owing to possible mixing across a diffuse entropy surface.

The Optics (Figure 1). Infrared transmitting windows of calcium fluoride were mounted flush with the inner walls of the shock tube. These are 2 in. in length and 10 mm. in width. The monochromator is a modified Perkin-Elmer instrument in which a 83 × 83 mm. B and L grating, 150 lines/mm., blazed at 6 μ for the first 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 six. 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-c.p.s. 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. Nevertheless, the effective rise time (particle coordinates) at the shock front, as recorded, was almost 10 μsec., due primarily to this passage time. For a signal/noise ratio of 15:1, the spectral resolution of this system as calibrated with HBr lines was found to be at 3195 cm.$^{-1}$ with slits 0.4–0.8 mm., 11.4 cm.$^{-1}$/mm. slit; at 2555 cm.$^{-1}$ with slits 0.5–0.7 mm., 7.3 cm.$^{-1}$/mm. slit. The design details of this system have been described[2]; as constructed its 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-l. 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 sulfuric 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.

(2) S. H. Bauer, N. C. Rol, and J. H. Kiefer in "Physical Chemistry in Aerodynamics and Space Flight," A. L. Meyerson and A. C. Harrison, Ed., Pergamon Press, New York, N. Y., 1961, p. 118.

Table I. Equilibrium Constants for the C_2H_2–D_2 Exchange Reaction

	$K_1 = \dfrac{(HD)^2}{H_2 \cdot D_2}$	$K_2 = \dfrac{C_2HD \cdot HD}{C_2H_2 \cdot D_2}$	$K_3 = \dfrac{(C_2HD)^2}{C_2H_2 \cdot C_2D_2}$	$K_4 = \dfrac{C_2D_2 \cdot HD}{C_2HD \cdot D_2}$
1600 °K.	3.9566	3.9764	3.8922	1.0216
1700 °K.	3.9619	3.9645	3.8934	1.0183

Equilibrium concn.[a]	C_2H_2	C_2HD	C_2D_2	D_2	H_2	HD
1600 °K.						
$\beta = 3.333$	0.053	0.352	0.595	1.970	1.184	0.179
$\beta = 2$	0.111	0.440	0.449	0.887	0.888	0.225
$\beta = 1$	0.251	0.497	0.252	0.250	0.499	0.251
$\beta = 0.5$	0.445	0.442	0.113	0.055	0.221	0.223
1700 °K.:						
$\beta = 3.333$	0.053	0.352	0.595	1.971	1.183	0.180
$\beta = 2$	0.111	0.440	0.449	0.887	0.888	0.225
$\beta = 1$	0.250	0.496	0.254	0.249	0.499	0.252
$\beta = 0.5$	0.444	0.442	0.114	0.055	0.221	0.224

[a] β is the ratio of the initial concentration of D_2 to C_2H_2.

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 (range in J, 0–80), based on the reported rotational constants for the ground and first excited vibrational states of acetylene.[3] These are illustrated in Figure 2. For
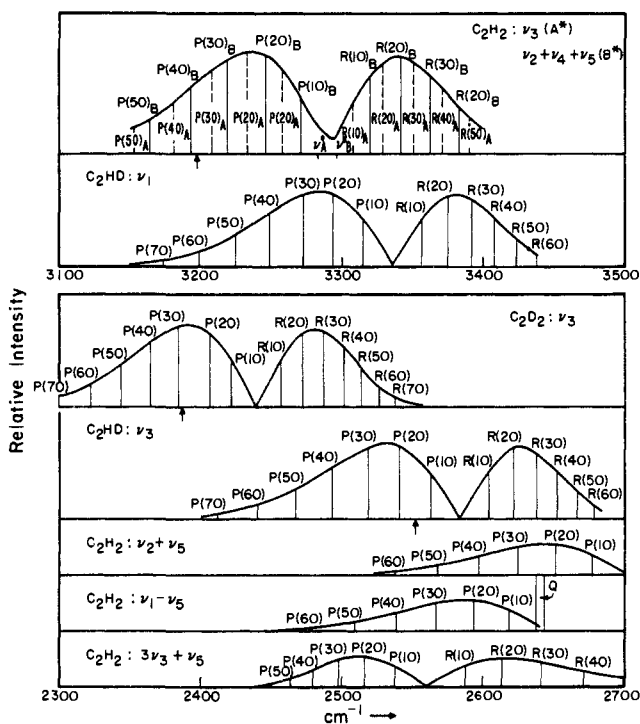

Figure 2. Theoretical envelopes showing the relative emission intensities of acetylene, monodeuterioacetylene, and dideuterioacetylene at 1700 °K.

estimating the concentration of acetylene present, we selected the frequency 3195 cm.$^{-1}$, at which the contribution by C_2H_2 exceeds by a factor of three that due to

(3) (a) M. T. Christensen, et al., Proc. Roy. Soc. (London), A238, 15 (1957); (b) H. C. Allen, et al., J. Am. Chem. Soc., 78, 3034 (1956); (c) J. Overend and H. W. Thompson, Proc. Roy. Soc. (London), A234, 3061 (1956); A232, 291 (1955).

C_2HD. At 2555 cm.$^{-1}$ the relative contribution due to C_2HD is largest; 2380–2390 cm.$^{-1}$ is clear for C_2D_2.

Quantitative calibrations were obtained at these selected frequencies. At $t = 0$ (immediately after passage of the shock) all the acetylene is present as C_2H_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 $t = 0$

$$I_0 = g[\epsilon(C_2H_2) \cdot c_0(C_2H_2)]\xi_{3195}$$

in which g represents the geometric factor of the optical and detecting system, ξ is the sensitivity of the photoconducting cell, c_0 is the initial concentration of the C_2H_2 (in moles/l.), and ϵ represents the emissivity of the gas at the shock temperature. Furthermore, at equilibrium ($t \rightarrow \infty$)

$$I_\infty = g[\epsilon(C_2H_2) \cdot c_\infty(C_2H_2) + \epsilon(C_2HD) \cdot c_\infty(C_2HD)]\xi_{3195}$$

At 3195 cm.$^{-1}$ the contribution to the emission by the fully deuterated acetylene is negligible. In the above equations it was assumed that the concentrations were sufficiently low so that no correction for self-absorption need be made. We then obtained the ratio I_∞/I_0, and, since the ratios of the concentrations of the species may be computed, the ratio $\epsilon(C_2HD)/\epsilon(C_2H_2)$ was evaluated.

$$\frac{I_\infty}{I_0} = \frac{c_\infty(C_2H_2)}{c_0(C_2H_2)} + \frac{\epsilon(C_2HD)}{\epsilon(C_2H_2)} \frac{c_\infty(C_2HD)}{c_0(C_2H_2)} \quad (1)$$

Typical data are given in Tables I and II. (The generally cited vibrational assignments are not self-consistent with an isotope invarient force field. This introduces small errors in the calculated equilibrium constants, as given in Table I.)

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

Table II. Experimental Determination of the Ratios of ε Values[a]

| | At 3195 cm.$^{-1}$ | | | At 2555 cm.$^{-1}$ | |
	(α)	(β)		(γ)	(δ)
I_∞/I_0	0.225	0.315	$I_\infty(C_2H_2 + D_2)$	25.4	27.0
			$I_0'(C_2H_2 + H_2)$	14.0	15.0
$c_\infty(C_2H_2)/c_0(C_2H_2)$	0.053	0.111		0.25	0.25
$c_\infty(C_2HD)/c_0(C_2H_2)$	0.352	0.440		0.50	0.50
$\epsilon(C_2HD)/\epsilon(C_2H_2)$	0.49	0.465		3.14	3.10
Av.	⟨0.48⟩			⟨3.12⟩	

[a] (α), average of four runs with $c_0(C_2H_2)/c_0(D_2) = 3.333$ at 1600–1700 °K.; (β), average of four runs with $c_0(C_2H_2)/c_0(D_2) = 2.00$ at 1550–1650 °K.; (γ) at about 1670 °K.; (δ) at about 1720 °K.

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

$$I_0'(C_2H_2 + H_2) = g[\epsilon(C_2H_2) \cdot c_0(C_2H_2)]\xi_{2555}$$

$$\frac{I_\infty(C_2H_2 + D_2)}{I_0'(C_2H_2 + H_2)} = \frac{c_\infty(C_2H_2)}{c_0(C_2H_2)} +$$
$$\frac{\epsilon(C_2HD)}{\epsilon(C_2H_2)} \frac{c_\infty(C_2HD)}{c_0(C_2H_2)} \quad (2)$$

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

$$I(3195) \propto [c(C_2H_2) + 0.48c(C_2HD)]$$
$$I(2555) \propto [c(C_2H_2) + 3.10c(C_2HD)] \quad (3)$$

Calculation of Shock Parameters. The gas temperature behind the incident shock (T_2) and the gas density ratio across the shock front (ρ_2/ρ_1) were computed from the measured shock velocities and the known enthalpies of the gaseous mixtures. The initial temperature was assumed to be 298 °K. No correction was made for the small enthalpy change due to 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 Cm.$^{-1}$). When a mixture of acetylene, hydrogen, and argon is shock heated to a temperature in the range 1300 to 1700 °K., the emission intensity rises sharply to a level which depends on the concentration of C_2H_2 owing to the compression by the shock and the vibrational excitation of acetylene to the first level. This emission remains constant over a period which depends on the incident shock temperature, before beginning to rise at a modest rate, indicating the onset of pyrolysis. This flat period is about 500 μsec. at 1300 °K. and decreases somewhat until at 1700 °K. the trace assumes a different shape. Then the emission intensity passes through a relatively narrow maximum before flattening out. These experiments are therefore limited to the indicated range of temperatures. 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 then slowly *decreases* with time. We interpret this decrease as being due to the conversion of some of the acetylene to deuterioacetylene. Additional experiments (described below) proved that the substitution reaction

was clean; no CH_4, C_2H_4, $C_2H_2D_2$, etc., were generated during the incident shock condition. The emitted intensity is proportional to the product of a geometrical factor, the sensitivity of the recording system, and the instantaneous concentration of the acetylenes. Let ρ_2^0 represent the gas density of acetylene immediately after passage of the shock. Then one may write

$$\frac{\rho_2^0}{I_0} \frac{dI}{dt} = \frac{d\rho(C_2H_2)}{dt} + \frac{\epsilon(C_2HD)}{\epsilon(C_2H_2)} \frac{d\rho(C_2HD)}{dt} \quad (4)$$

for the rate of change in emission with time. Note that in the analysis given below only 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 (ρ_2/ρ_1) to convert the "laboratory" reaction time to particle time. The initial reaction rate constant is then defined by the equation

$$R_\alpha \equiv -\frac{\rho_2^0}{I_0}\left(\frac{\Delta I}{\Delta t}\right)_0 = k_\alpha(C_2H_2)_0^n(D_2)_0^m(Ar)_0^l \quad (5a)$$

It will be shown below that the rate of increase of C_2HD is directly proportional to the rate of decrease of C_2H_2. Hence, in eq. 4 both terms of the right member are proportional to $d\rho(C_2H_2)/dt$. In the first step a single rate constant was evaluated from the emission at 3195 cm.$^{-1}$.

To establish the reaction order for this exchange with respect to D_2, values of R_α were plotted against the reciprocal of the temperature 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 3). 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 $R_\alpha/\rho_2^0(D_2)$ were plotted against the reciprocal of the absolute temperature. 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 $R_\alpha/\rho_2^0(D_2)$ were individually plotted (for T_1, T_2, and T_3) against the logarithm of the density of acetylene. The slopes vary somewhat with temperature; they are, respectively, $n = 0.29 \pm 0.01$ at 1350 °K.; 0.20 ± 0.03 at 1455 °K.; 0.23 ± 0.03 at 1612 °K. We have adopted the average $n = 0.24$.

The over-all order for the exchange reaction as measured by the rate of disappearance of the C_2H_2
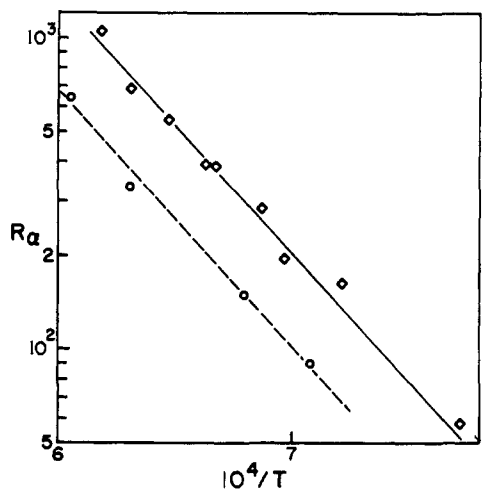
Figure 3. Logarithmic plot of R_α vs. $10^4/T$ for runs with constant (C_2H_2) and (Ar), but $(D_2)_0$ differs by a factor of two: solid line, $C_2H_2/D_2/Ar = 10:10:80$; dashed line, $C_2H_4/D_2/Ar = 10:5:85$.
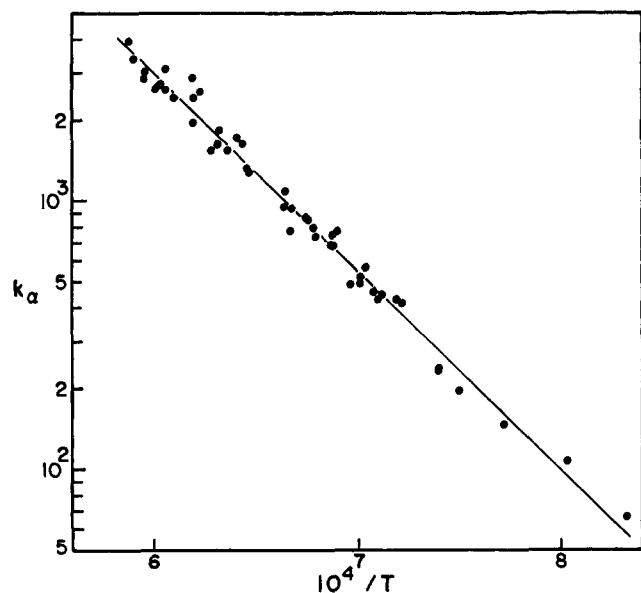

Figure 4. Plot of the rate constant for the disappearance of C_2H_2, due to reaction with D_2, as measured from the decline in emission intensity at 3195 cm.$^{-1}$ vs. the reciprocal temperature: $C_2H_2/D_2/Ar = 10:10:80$; $5:10:85$; $3:10:87$; and $10:5:85$; total density variation by a factor of five.

Figure 5. Plot of the rate constant for the production of C_2HD, as measured from the rise in emission intensity at 2555 cm.$^{-1}$ vs. reciprocal temperature: range covered (in concentrations and densities) is the same as in Figure 4.

$$R_\alpha = k_\alpha(C_2H_2)_0^{0.24}(D_2)_0^{1.0}(Ar)_0^0 \qquad (5b)$$

temperature (Figure 4). The deduced activation energy is $E_\alpha = 33.8 \pm 0.4$ kcal./mole, and the corresponding $A = (8 \pm 1) \times 10^7$ (mole/l.)$^{-0.24}$ sec.$^{-1}$, for the rate of disappearance of acetylene due to reaction with deuterium, in the temperature range 1200 to 1700°K. Table III is a summary of typical conditions for nine out of the fifty runs shown in Figure 4. For each composition the lowest and highest temperatures were selected. In contrast with eq. 5, the D–H exchange rate for the reaction between NH_3 and D_2 is zero order in ammonia and first order in argon.

Kinetics of Production of C_2HD (as Measured by Emission at 2555 Cm.$^{-1}$). The procedure for measuring the growth of the 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 slight complexity. The acetylene originally present in the shock gas produced, on compression and heating, a considerable emission which showed up as a steep rise 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°K. after this rapid initial rise covering a period of about 20 μsec., there followed an almost linear slower increase due to the production of C_2HD by the exchange reaction. Above 1600°K. the inflection point could not be easily detected; hence the data cited below were restricted to runs made below that temperature. Again it was established that the order of the reaction was unity with respect to the initial deuterium concentration. As tested previously, $R_\beta/\rho_2^0(D_2)$ values were plotted against the reciprocal temperature, and the points were corrected to the reference temperature of 1470°K. The reduced $R_\beta/\rho_2^0(D_2)$ 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 ± 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

was then obtained from a series of experiments corrected to a single temperature, in which the total density was changed by a factor of five 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 we chose to be the density of the acetylene. The slope of a plot of the logarithm 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 0.53×10^{-3} to 2.51×10^{-3} gave at 1455°K. a value for $(n + m + 1) = 1.20 \pm 0.05$. 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_α as evaluated on the basis of the eq. 5b was plotted against the reciprocal of the absolute
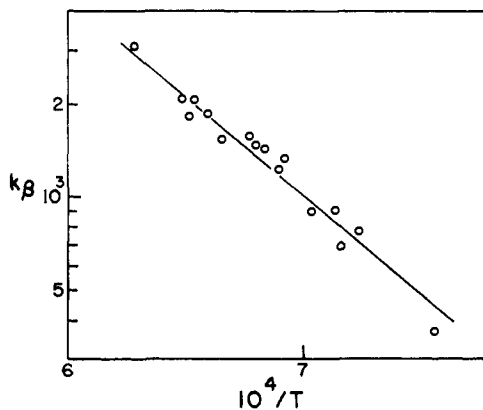
Table III. Typical Data for the 3195-Cm.⁻¹ Band

	← Composition of $C_2H_2/D_2/Ar$ →								
	←——10:10:80——→			←——5:10:85——→		←——3:10:87——→		←——10:5:85——→	
p_1 (total), mm.	26	82	41.5	80	80	61	61	81	43
$p_2^0(C_2H_2)^a$	0.59×10^{-3}	1.91×10^{-3}	0.99×10^{-3}	0.78×10^{-3}	0.87×10^{-3}	0.34×10^{-3}	0.378×10^{-3}	1.80×10^{-3}	1.01×10^{-3}
$p_2^0(D_2)$	0.59×10^{-3}	1.91×10^{-3}	0.99×10^{-3}	1.57×10^{-3}	1.74×10^{-3}	1.14×10^{-3}	1.26×10^{-3}	0.90×10^{-3}	0.51×10^{-3}
T_2, °K.	1390	1545	1665	1245	1680	1200	1700	1410	1695
p_2/p_1	4.19	4.34	4.44	3.65	0.01	3.47	3.83	4.12	4.35
R_α^b	0.0422	0.545	0.489	0.0306	0.970	0.0111	0.753	0.0900	0.329
$R_\alpha/p_2^0(D_2)$	0.715×10^2	2.85×10^2	4.96×10^2	0.195×10^2	5.59×10^2	0.0975×10^2	5.98×10^2	1.00×10^2	6.45×10^2
k_α^c	0.426×10^3	1.28×10^3	2.61×10^3	0.109×10^3	3.04×10^3	0.0655×10^3	3.94×10^3	0.455×10^3	3.36×10^3

ᵃ p_2 is the corresponding gas density (mole/l.) immediately after passage of shock. ᵇ $R_\alpha \equiv p_2^0/I_0 (\Delta I/\Delta t)_0(p_1/p_2)$, in mole l.⁻¹sec.⁻¹. ᶜ $k_\alpha = R_\alpha/p_2^0 \cdot (D_2)p_2^0(C_2H_2)^{0.24}$, in (l./mole)⁰·²⁴ sec.⁻¹.

conditions of our experiment follow the same functional dependence on the initial concentrations of reactants (eq. 5). A plot of the reduced rate constant against the reciprocal of the temperature (Figure 5) gave for the activation energy $E_\beta = 29.3 \pm 1.1$ kcal./mole; the corresponding $A = 3 \times 10^7$ (mole/l.)⁻⁰·²⁴ sec.⁻¹. The limits of error quoted for E_α and E_β are based on the internal consistency of each set of runs; on an absolute basis we consider these activation energies to be approximately equal, except for differences in effective zero-point energies.

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 (α) 3195 cm.⁻¹ and at (β) 2555 cm.⁻¹, to obtain absolute rates by noting the relative contributions of each species to the intensities recorded at these frequencies.

$$-k_\alpha(C_2H_2)^{0.24}(D_2) = \frac{d(C_2H_2)}{dt} +$$

$$\left[\frac{\epsilon(C_2HD)}{\epsilon(C_2H_2)}\right]_\alpha \frac{d(C_2HD)}{dt} = \frac{d(C_2H_2)}{dt} + 0.48 \frac{d(C_2HD)}{dt}$$

$$\text{(6)}$$

$$k_\beta(C_2H_4)^{0.24}(D_2) = \frac{d(C_2H_2)}{dt} +$$

$$\left[\frac{\epsilon(C_2HD)}{\epsilon(C_2H_2)}\right]_\beta \frac{d(C_2HD)}{dt} = \frac{d(C_2H_2)}{dt} + 3.12 \frac{d(C_2HD)}{dt}$$

On rearranging terms

$$-\frac{d(C_2H_2)}{dt} = k_{C_2H_2}(C_2H_2)^{0.24}(D_2) =$$

$$\frac{3.12k_\alpha + 0.48k_\beta}{3.12 - 0.48}(C_2H_2)^{0.24}(D_2)$$

$$\text{(7)}$$

$$\frac{d(C_2HD)}{dt} = k_{C_2HD}(C_2H_4)^{0.24}(D_2) =$$

$$\frac{k_\alpha + k_\beta}{3.12 - 0.48}(C_2H_2)^{0.24}(D_2)$$

Specifically, at 1470°K.

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

$$\text{(8)}$$

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

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 one-third of the C_2H_2 leads to the production of C_2D_2. The rate of production of C_2D_2 is then roughly one-half that of C_2HD.

To substantiate this conclusion we cite rough analytical data obtained in a single-pulse experiment on a sample of composition and temperature comparable to that used for the infrared runs.[4] Mass spectrometric analysis of a shocked mixture of $C_2H_2 + D_2$ showed: (a) the amount of H_2 generated was definitely less but comparable to that of HD; (b) the decrease in the amount of C_2H_2 was larger than the amount of C_2HD generated; and (c) no methane or ethylene (C_2H_4 or $C_2H_2D_2$) was produced. A few preliminary infrared runs at 2380 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.

Discussion of Mechanism

There appear to be no previous successful attempts to measure the homogeneous gas phase reaction between acetylene and deuterium. Coats and Anderson[5] heated equimolar mixtures of the two gases in 25-ml. bulbs for 2–10 min. to 500–900°, at a total initial pressure of 300 mm. 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[6] and as induced by radiations which generate atoms. In the latter, the primary attack is an atomic displacement or an abstraction.[7] The pyrolysis of

(4) We are indebted to Assa and Chava Lifshitz for this experiment.
(5) F. H. Coats and R. C. Anderson, AFOSR TN-56-491 (AD 110-305), University of Texas, Oct. 1956, under AF18(600)-430, Chem. 50-1.
(6) G. C. Bond, *Trans. Faraday Soc.*, **52**, 1235 (1956).
(7) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. 1, 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1954, p. 419 ff; L. Kaplan, *J. Am. Chem. Soc.*, **76**, 1448 (1954); R. E. Varnerin, *et al.*, Division of Petroleum Chemistry, 127th National Meeting of the American Chemical Society, March 1955, Cincinnati, Ohio, Paper No. 22.

Figure 6. Proposed sequence of configurations for the H/D exchange: read from upper left, down, and toward upper right.

acetylene in shock tubes has been investigated.[8] The temperatures used in our experiments (in the incident shock region) were several hundred degrees below those needed for the pyrolysis studies.

The observation that for the exchange reaction the activation energy is so low (≈ 33 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[9] and of $C_2H_2 \rightarrow C_2H + H$. The fact that the rate of production of C_2D_2 is about half that of C_2HD suggests that these species are derived from the same transition state, which we designate $C_2H_2D_2{}^*$. Finally, the observation that the rate does depend on a small fractional power of the acetylene concentration argues for quenching reactions, selectively sensitive to C_2H_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 excited ethylene, with V_d symmetry, approximately 3.3. e.v. above the ground state [$E_\alpha + \Delta H_{\text{hydrog}}(C_2H_2) \approx 3.3$ e.v.]. It is assumed that species in this state have a much greater probability for dissociation than for internal conversion to stable ethylene.[10] The formal rate expression is based on the sequence

$$C_2H_2 + D_2 \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} C_2H_2 \cdot D_2$$

$$C_2H_2 \cdot D_2 + C_2H_2 \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} 2C_2H_2 + D_2$$

$$C_2H_2 \cdot D_2 \underset{k_3}{\overset{k_{-3}}{\rightleftharpoons}} C_2H_2D_2{}^*$$

(8) (a) C. F. Aten and E. F. Greene, Discussions Faraday Soc., 22, 162 (1956); (b) S. S. Penner, et al., AGAR Dograph No. 61, "Fundamental Data Obtained from Shock Tube Experiments," A. Ferri, Ed., Pergamon Press, New York, N. Y., 1961, pp. 183, 219; (c) J. N. Bradley, "Shock Waves in Chemistry and Physics,"John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 128, 267, 321, 325.

(9) J. P. Rink, J. Chem. Phys., 36, 1398 (1963).

(10) This is entirely compatible with the known equilibrium constants and rate of conversion of ethylene to acetylene and hydrogen, at these temperatures: G. B. Skinner and E. M. Sokoloski, J. Phys. Chem., 64, 1028 (1960). We thank Dr. Skinner for a helpful discussion of this point.

$$C_2H_2D_2{}^* \xrightarrow[2k_{-3}]{} C_2HD \cdot HD \xrightarrow[k_{-1}]{} C_2HD + HD$$
$$k_2(C_2H_2)$$

$$C_2H_2D_2{}^* \xrightarrow[k_{-3}]{} C_2D_2 \cdot H_2 \xrightarrow[k_{-1}]{} C_2D_2 + H_2$$
$$k_2(C_2H_2)$$

The production of $C_2H_2 \cdot D_2$ via (-2) may be neglected because it is a three-body process; it appears that Ar is not an effective third body for (1), and hence is correspondingly ineffective for (-1). Also, during the initial stages of the reaction, the reverse steps involving C_2HD and C_2D_2 are negligible. Schematically, the sequence of structures is diagramed in Figure 6.

On applying the steady-state condition to the transient species $C_2HD \cdot HD$, $C_2H_2D_2{}^*$, and $C_2H_2 \cdot D_2$, one readily derives

$$\frac{d(C_2HD)}{dt} = \frac{k_1 k_3 \alpha}{2k_2} \frac{(D_2)(C_2H_2)}{1 + \alpha(C_2H_2)} \tag{9}$$

where $\alpha = k_2/(k_{-1} + 0.75k_3)$ (mole^{-1} l.). For the initial rate of production of C_2D_2 a similar expression follows, but the coefficient is $k_1 k_3 \alpha/4k_2$. For the initial rate of depletion of C_2H_2, the identical functional dependence is obtained, with the coefficient $3k_1 k_3 \alpha/4k_2$. The measured rate constant in eq. 7 is thus identified with

$$k_{C_2H_2} = 0.75 \frac{k_1 k_3 (C_2H_2)^{0.76}}{k_{-1} + 0.75k_3 + k_2(C_2H_2)}$$

It is evident that the net power dependence of $d(C_2H_2)/dt$ on the acetylene concentration could range from unity to zero, depending on the magnitude of $\alpha(C_2H_2)$ relative to unity; that is, on the relative efficiency for depletion of $C_2H_2 \cdot D_2$ via collisions with C_2H_2 compared with that by decomposition and rearrangement.

To test eq. 9 in detail, it is convenient to accept the postulate that the rate of production of C_2HD is directly proportional to the rate of destruction of C_2H_2. Write

$$\frac{d(C_2HD)}{dt} = -\frac{2}{3}\Theta\frac{d(C_2H)_2}{dt} \tag{10}$$

where the proportionality constant Θ, if it differs from unity, measures the departure from a strictly statistical process for the dissociation of $C_2H_2D_2{}^*$. Then eq. 6 may be written

$$R_\alpha = -\frac{d(C_2H)_2}{dt}[1 - 0.32\Theta] =$$

$$(1 - 0.32\Theta)\frac{3k_1 k_3}{4k_2}\frac{\alpha(D_2)(C_2H_2)}{1 + \alpha(C_2H_2)} \tag{11}$$

$$R_\beta = \frac{d(C_2HD)}{dt}[3.12 - 1.5/\Theta] =$$

$$(3.12 - 1.5/\Theta)\frac{2k_1 k_3}{4k_2}\frac{\alpha(D_2)(C_2H_2)}{1 + \alpha(C_2H_2)}$$

Let $\Omega \equiv (D_2)_0(C_2H_2)_0/R_\alpha$. Then, for any one shock temperature, a plot of Ω vs. $(C_2H_2)_0$ should be a straight line with a slope equal to $4k_2/3k_1 k_3(1 - 0.32\Theta)$ and an intercept equal to $1/\alpha$ times the slope. The reduced data used above to establish the value of n in eq. 5 for the empirical power law were plotted in Figure 7a,b,c. The points are consistent with a linear dependence, to within the random errors of this experi-
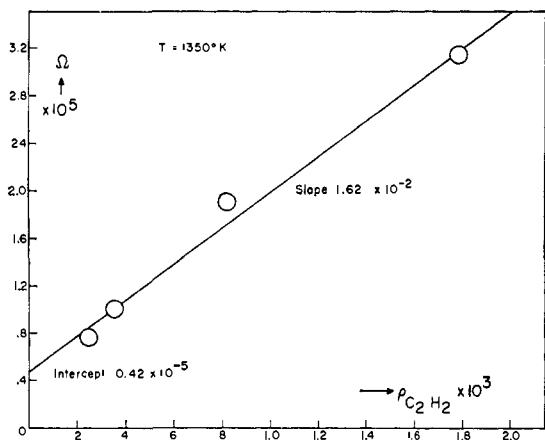
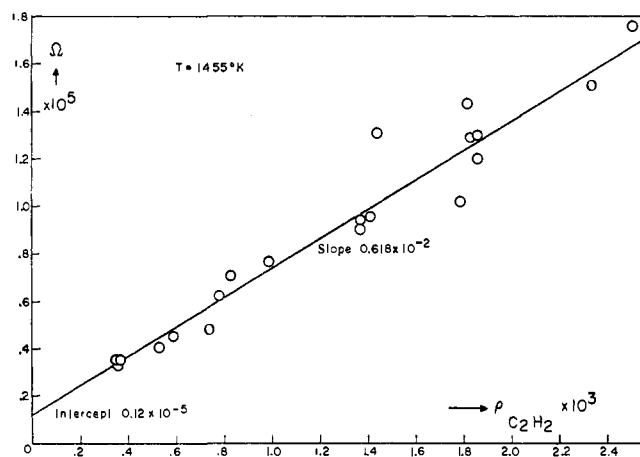Figure 7a. Graph of the function Ω vs. the initial concentration of acetylene at 1350°K.

Figure 7b. Graph of the function Ω vs. the initial concentration of acetylene at 1455°K.
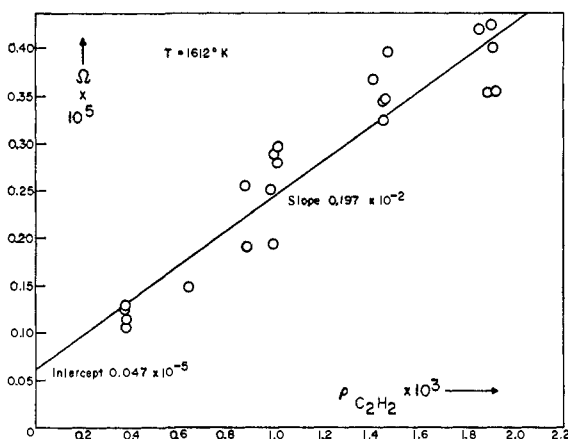

Figure 7c. Graph of the function Ω vs. the initial concentration of acetylene at 1612°K.

ment. The derived values are listed in Table IV. Whereas the slopes and intercepts depend sensitively on the temperature, their ratio remains essentially constant to within the precision of these extrapolations. An average value $\langle\alpha\rangle = 3.93 \times 10^3$ mole^{-1} l. was adopted; it measures the high quenching efficiency of $C_2H_2 \leftrightarrow C_2H_2 \cdot D_2$ collisions. A plot of the logarithm of $R_\alpha/\{\langle\alpha\rangle(D_2)_0(C_2H_2)_0/[1 + \langle\alpha\rangle(C_2H_2)_0]\}$ vs. $10^4/T$ (Figure
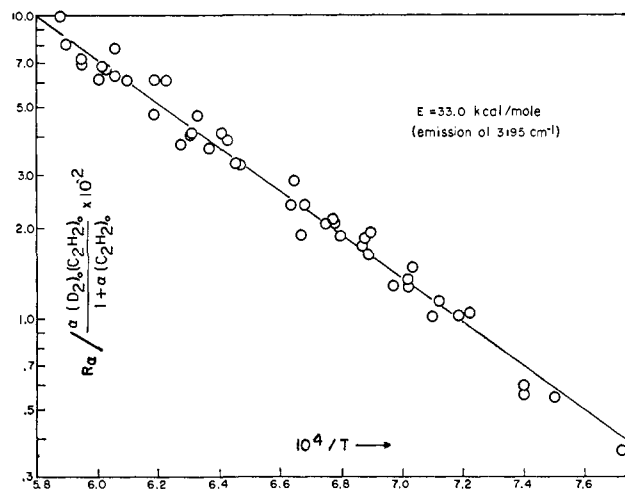
Figure 8. Substitution rates, deduced from the rate of decline in emission intensity, at 3195 cm.$^{-1}$, plotted against the reciprocal temperature (eq. 9; $\langle\alpha\rangle = 3.93 \times 10^3$); compare with Figure 4.

8) gave an effective activation energy of 33.0 kcal./mole. With the same value of $\langle\alpha\rangle$, the emission data at 2555 cm.$^{-1}$ were used to compute $R_\beta/\{\langle\alpha\rangle(D_2)_0(C_2H_2)_0/[1 + \langle\alpha\rangle(C_2H_2)_0]\}$, and plotted vs. $10^4/T$ (Figure 9).
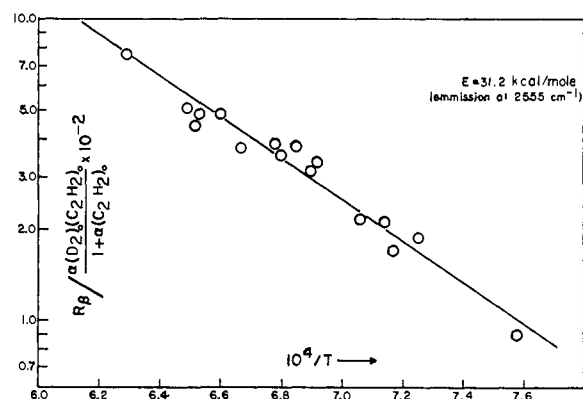

Figure 9. Substitution rates, deduced from the rate of increase in emission intensity at 2555 cm.$^{-1}$, plotted against the reciprocal temperature (eq. 9; $\langle\alpha\rangle = 3.93 \times 10^3$); compare with Figure 5.

The best straight line has a slope which gives for the activation energy 31.2 kcal./mole. Because of the larger temperature range covered and the greater number of data points available in Figure 8, we propose that the effective activation energy for the homogeneous H–D exchange in acetylene is 32.5 ± 1.0 kcal./mole. Then, from 3195 cm.$^{-1}$

$$0.75\,(\,1 - 0.32\Theta)\frac{k_1 k_3}{k_2} =$$

$$1.41 \times 10^7 \exp(-32{,}500/RT) \quad (12a)$$

and from 2555 cm.$^{-1}$

$$0.50\,(3.12 - 1.5/\Theta)\frac{k_1 k_3}{k_2} =$$

$$2.35 \times 10^7 \exp(-32{,}500/RT) \quad (12b)$$

These equations lead to $\Theta = 1.05$; a number somewhat less than unity was expected because of the kinetic isotope effect. However, we are comparing here two

Table IV. Values for Slopes and Intercepts Derived from Figure 6[a]

Temp., °K.	Slope × 10^2, sec.	Intercept × 10^5, mole l.$^{-1}$ sec.	α × 10^{-3} mole^{-1} l.
1350	1.62	0.42	3.09
1415	0.618	0.12	5.73
1612	0.197	0.047$_5$	2.98

[a] Emission data at 3195 cm.$^{-1}$; $\langle\alpha\rangle$ = 3.93 × 10^3 mole^{-1} l.

sets of shock tube data taken over a long period of time, wherein two distinct calibrations for emission intensi- ties are involved. We must conclude that Θ is essentially unity within our absolute error. Equation 12 leads to

$$\frac{k_1 k_3}{k_2} = 2.8 \times 10^7 \exp(-32{,}500/RT) \ (\text{mole}^{-1} \ \text{l. sec.}^{-1})$$

One may argue that the association rate (1) probably has a collision efficiency of 10^{-1} to 10^{-2}, while the quenching step (2) has unit collision efficiency. This leads to an internal conversion efficiency (step 3) of 10^{-3} to 10^{-2}, which is inherently reasonable.

The Thermal Unimolecular Isomerization of Methyl-d_1 Isocyanide. Fall-Off and Inverse Isotope Effect[1]

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Earlier work (parts I and II) on the study of methyl and methyl-d_3 isocyanides has been extended to the methyl-d_1 compound. A brief study has been made of the fall-off at 245° at pressures from 9.3 atm. down to 0.05 mm., and values of k/k_∞ from ~1 down to 0.0042. No significant effect on the fall-off behavior due to the splitting of the four doubly degenerate modes of methyl isocyanide by the deuterium substituent is observed; the variation of fall-off behavior for the three compounds, methyl, methyl-d_1, and methyl-d_3 isocyanides, are as expected from differential quantum statistical factors. With decrease of pressure an inverse statistical-weight isotope effect is found which is in good agreement with the theoretical formulation in II; k_{CH_3}/k_{CH_2D} is measured as 0.75 at the lowest pressure studied and is extrapolated down to ~0.70; the limiting low pressure value is calculated to be $(k_{CH_3}/k_{CH_2D})_0 = 0.67$, on a quantum statistical basis. At the high pressure limit, $k_{CH_3}/k_{CH_2D} \simeq 1$, as expected.

Introduction

The thermal unimolecular isomerization of methyl[2a] and methyl-d_3[2b] isocyanide has been reported earlier. In continuation of the study of the isocyanide reaction system, the methyl-d_1 isocyanide system has now been examined. Unlike the methyl-d_3 molecule which has C_{3v} symmetry similar to the light methyl compound, monodeuteration introduces a new structural feature by splitting the degeneracy of the four doubly degenerate modes, a C–H stretch, a methyl rock and methyl deformation, and the skeletal bend.

This molecule also provides another potential example of the inverse intermolecular secondary isotope

effects described earlier for nonequilibrium (*i.e.*, low pressure conditions) thermal systems.[3] The present study is brief, but adequate for illustrating the differential quantum effects in this series of isotopically substituted molecules.

Experimental

Materials. CDH₂NC was prepared by allowing CDH₂I (from Merck Sharp and Dohme, Ltd., Montreal) to react with silver cyanide in the molar ratio 1:2 by the modified Gautier method.[2a] It was purified by gas chromatography on a tetraglyme–Fluoropak column. The isotopic purity of the material was determined by parent peak analysis with a Consolidated 21–103 mass spectrometer and was found to contain 3.4% CH₃NC. Acetonitrile was also purified on the gas chromatographic column.

Procedure. An internal comparison method similar to that described in II was employed. A reactant mixture of CH₃NC and CH₂DNC of composition 3:1 was prepared under mercury-free conditions, by using a glass diaphragm click gauge. Runs were carried out in a conventional high vacuum apparatus at an average temperature of 245°. Reaction vessels of different sizes varying from 0.8 ml. at the highest pressure up to 12 l. at the lower pressures were used. No corrections were necessary for small deviation from the average temperature because of the negligible temperature coefficient found in II for this isotope effect. Temperature over the reactors was usually constant to ±0.5° in the worst case. The vessels were seasoned and "exchanged" before use, as in II. The conversion of reactants was kept as low (average 20%) as was convenient for analysis.

In the run at highest pressure, 1.14 × 10⁴ mm., in order to conserve reactant the vessel was pressurized

(1) This work was supported by the National Science Foundation.
(2) (a) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, 84, 4215 (1962), called I; (b) *ibid.*, 85, 2365 (1963), called II. In II, on p. 2366, right column, second paragraph, line 4, *ten* decades should be replaced by *six* decades.

(3) B. S. Rabinovitch, D. W. Setser, and F. W. Schneider, *Can. J. Chem.*, 39, 2609 (1961).