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The Reaction of Hydrogen Atoms with Acetylene

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The addition of hydrogen atoms to acetylene has been investigated at room temperature. The relative rate constant for

$$\mathrm{H} + \mathrm{C_2H_4} \longrightarrow \mathrm{C_2H_5}, \qquad (1)$$
$$\mathrm{H} + \mathrm{C_2H_2} \longrightarrow \mathrm{C_2H_3}, \qquad (2)$$

was found to be $k_1/k_2=9.99\pm0.16$. The ratios of the rate constant of disproportionation to that of the combination for the same radicals and for different radicals were determined to be as follows:

$$\mathrm{C_2H_5} + \mathrm{C_2H_3} \longrightarrow \text{1-}\mathrm{C_4H_8}, \qquad (4)$$
$$\longrightarrow \mathrm{C_2H_6} + \mathrm{C_2H_2}, \qquad (4a)$$
$$\longrightarrow 2\mathrm{C_2H_4}, \qquad (4b)$$
$$k_{4a}/k_4 = 0.369,$$
$$k_{4b}/k_4 = 0.68,$$
$$\mathrm{C_2H_3} + \mathrm{C_2H_3} \longrightarrow \text{1,3-}\mathrm{C_4H_6}, \qquad (5)$$
$$\longrightarrow \mathrm{C_2H_4} + \mathrm{C_2H_2}, \qquad (5a)$$
$$k_{5a}/k_5 = 0.087.$$

Although a large amount of quantitative data is now available on the addition of atomic hydrogen to simple olefins,[1-3] comparatively little is known about the reactions of unsaturated radicals, probably because of the difficulty of obtaining clean sources of these radicals, and also because of the problems in analysis, *i.e.*, the polymerization of an unsaturated radical.[4]

Recently, however, Hoyermann, *et al.*[5] have produced a vinyl radical by the addition of a hydrogen atom to acetylene and proposed a rate constant of: 2.3×10^{12} $\exp(-2500\ \mathrm{cal\ mol^{-1}}/RT)$ for the addition reaction. Cowfer, *et al*[6]. have obtained the ratios of the rate constants for H atom-olefin reactions to that for the H atom–acetylene system. In spite of quantitative studies[7-11] which have been published concerning the reactions of vinyl radicals, the data for the ratio of the disproportionation to the combination of the radicals show large discrepancies (see the last column of Table 2), and it remains difficult to say which value should be preferred.

In the present work, we have employed the competitive technique developed for determining the relative rate constants of the reactions of hydrogen atoms with olefins;[3] we have thus determined the relative rate constant of the addition of H atoms to acetylene and the ratio of the disproportionation to the recombination of vinyl radicals. Similar ratios of reactions between vinyl and ethyl radicals have also been obtained.

Experimental

Hydrogen atoms were generated by the $\mathrm{Hg}6(^3P_1)$ sensitized decomposition of H_2. The 2537 Å radiation was obtained from a low-pressure mercury lamp with a Vycor glass filter. A conventional vacuum apparatus was used.

The acetylene and ethylene were purchased from the Takachiho Co.; both gases contained methane and ethane as impurities. The acetylene and ethylene were purified by a gas chromatograph provided with a 1.75 m activated charcoal column at 200 °C, and with a 0.7 m Molecular Sieves 13X column at 200 °C, respectively. The purified gases contained no impurity within the limits of sensitivity of a gas chromatograph with a flame ionization detector; therefore, both gases had a minimum purity of 99.999%. Takachiho research-grade hydrogen (99.999 vol%. O_2 content less than 0.1 ppm) was used without further purification.

The experiments were carried out at 22.7±1.0 °C, and the reactant-product mixture was analyzed by means of a gas chromatograph using a 4 m column of phenylisocyanate on Poracil C (Waters Associates, Inc.,) at 30 °C, and a flame ionization detector. The benzene was measured using a 2 m column of dioctylphthalate, followed by a 2 m column of polyethyleneglycol-4000 on Celite 545 at 80 °C.

In order to compare the rate constant for the $\mathrm{H}+\mathrm{C_2H_2}$ reaction with that for the $\mathrm{H}+\mathrm{C_2H_4}$ reaction in the photolysis of the $\mathrm{H_2}$–$\mathrm{C_2H_2}$–$\mathrm{C_2H_4}$ system, it is necessary to determine the rate of the formation of the *n*-butane which would be formed if acetylene was absent in the system (denoted by $r_B{}^*$). Thus, the rate of butane formation was monitored by using two reaction cells, a "mixture" cell (203 ml) and a "reference" cell (204 ml), under identical photolytic conditions. At first, the same pressures of ethylene (3.4—32.5 Torr) and hydrogen (~630 Torr) were admitted simultaneously to both cells, each containing a few drops of mercury, and then the cells were illuminated by an identical light source. Thus, the ratio of the rates of the formation of *n*-butane: $R_{n\text{-}\mathrm{C_4H_{10}}}$ (Mixture cell)/$R_{n\text{-}\mathrm{C_4H_{10}}}$ (Reference cell), was obtained in the $\mathrm{H_2}$–$\mathrm{C_2H_4}$ system; we define it as the "reference ratio."

Next, in the main run, the same pressures of ethylene (15—30 Torr) and hydrogen (~630 Torr) were put into both cells, while various pressures of acetylene were added to the "mixture cell." Then photolysis was performed in the same way as in the preliminary run. Thus, the value of $r_B{}^*$ was calculated by means of the following relation:

$$r_B^* = (\text{reference ratio}) \times (\text{the rate of } n\text{-butane formation in the reference cell in the main run}).$$

The reference ratio was checked both before and after the photolysis of the $\mathrm{H_2}$–$\mathrm{C_2H_2}$–$\mathrm{C_2H_4}$ system; if the two values differed, the mean value was used in the calculation.

TABLE 1. DATA FOR Hg-PHOTOSENSITIZED REACTION OF C_2H_2–C_2H_4–H_2 MIXTURES

Reactants (Torr at 22.7 °C)			Photolysis time (min)	C_4H_{10} yield (μM)		Reference[a)] ratio	Products (n-C_4H_{10}=1.000)			
C_2H_2	$\frac{C_2H_2}{C_2H_4}$	H_2		Reference cell	Mixture cell		C_2H_6	1-C_4H_8	1,3-C_4H_6	C_6H_6
20.98	2.36	622.9	60[b)]		2.197		0.231	0.152	0.091	0.013
25.45	4.50	624.4	60[b)]		1.292		0.302	0.363	0.180	0.056
23.8	4.53	630.3	60[b,c)]		0		0	0	0	0
0	0	~630	5.0				0.157±0.002[d)]			
13.27	0.742	638.0	5.0	2.682	2.365	1.020	0.182	0.074	—	
18.92	1.648	640.9	5.0	2.382	3.979	2.301	0.225	0.076	0.023	
21.37	2.803	629.7	5.0	2.185	1.304	0.988	0.287	0.277	0.090	
21.97	3.898	628.8	5.0	3.162	1.708	0.985	0.323	0.389	0.139	
25.37	4.456	619.5	5.0	2.082	1.063	1.073	0.338	0.413	0.194	
24.96	5.186	634.9	3.0	1.890	0.795	0.971	0.411	0.701	0.260	
27.00	7.105	626.3	5.0	3.538	1.396	1.154	0.436	0.661	0.525	

a) Reference ratio=$R_{C_4H_{10}}$(Mixture)/$R_{C_4H_{10}}$ (Reference). See text. b) Incident light was reduced to about one tenth. c) 2.0 Torr of NO was added. d) Mean value of 15 experiments. Pressure of ethylene was varied from 3.4 to 32.5 Torr.

Results and Discussion

In a series of experiments designed to ascertain the rate measurements, the H_2 pressure was kept higher than 600 Torr and constant. The total olefin pressure was very much smaller than the hydrogen pressure and was also kept approximately constant (~30 Torr). The products were ethane, n-butane, 1-butene, 1,3-butadiene, benzene, and negligible amounts of propane and propylene. The relative rate of the formation of each product is given in Table 1.

Now, if ethylene or acetylene quenches $Hg6(^3P_1)$ atoms and undergoes chemical reactions, acetylene and benzene should be formed from excited ethylene[12)] and acetylene[13)] respectively. On the other hand, in the experiments with the mixtures of ethylene (3.4—32.5 Torr) and hydrogen (~630 Torr), no acetylene was detected. Table 1 also shows that benzene formation is suppressed in the H_2–C_2H_2–C_2H_4 system by the addition of a small amount NO, which is known to suppress radical reactions. These observations imply that the excited olefin molecules formed by quenching are efficiently deactivated in collisions with other molecules present, without undergoing a chemical reaction.

The C_2H_6/n-C_4H_{10} ratio in the H_2–C_2H_4 system is very close to the normal ratio of the disproportionation to the combination of ethyl radicals, 0.13—0.14.[14)] This shows that the H atom-radical reaction is negligible:

$$H + C_2H_5 \longrightarrow C_2H_6.$$

The formation of products may be explained by the following competitive reactions:[3)]

$$\begin{aligned}
Hg6(^1S_0) + h\nu(2537\,\text{Å}) &\longrightarrow Hg6(^3P_1), && \text{(a)}\\
H_2 + Hg6(^3P_1) &\longrightarrow 2H + Hg6(^1S_0), && \text{(b)}\\
H + C_2H_4 &\longrightarrow C_2H_5, && (1)\\
H + C_2H_2 &\longrightarrow C_2H_3, && (2)\\
C_2H_5 + C_2H_5 &\longrightarrow n\text{-}C_4H_{10}, && (3)\\
&\longrightarrow C_2H_6 + C_2H_4, && \text{(3a)}\\
C_2H_5 + C_2H_3 &\longrightarrow 1\text{-}C_4H_8, && (4)\\
&\longrightarrow C_2H_6 + C_2H_2, && \text{(4a)}\\
&\longrightarrow 2C_2H_4, && \text{(4b)}\\
C_2H_3 + C_2H_3 &\longrightarrow 1,3\text{-}C_4H_6 && (5)\\
&\longrightarrow C_2H_4 + C_2H_2, && \text{(5a)}\\
C_2H_3 + C_2H_2 &\longrightarrow C_4H_5, && (6)\\
C_4H_5 + C_2H_2 &\longrightarrow C_6H_7, && (7)\\
C_6H_7 &\longrightarrow C_6H_6 + H, && (8)\\
C_4H_5 + nC_2H_2 &\longrightarrow \text{polymer}, && (9)
\end{aligned}$$

where Reactions 6—9 have been proposed by Tsunashima and Sato.[13)]

In the competitive reaction technique, the basic premise is that the rates of the mutual interaction of the radicals formed are determined statistically:[3)]

$$k_5 + k_{5a} = f(k_3 + k_{3a}).$$

If f happens to be unity, and if the simple collision theory of chemical kinetics can be applied to Reactions 3—5a, the activation energies of which are considered to be small,[15)] one can get the following equation:

$$k_4 + k_{4a} + k_{4b} = 2(k_3+k_{3a}) = 2(k_5+k_{5a}) = 2k. \qquad \text{(A)}$$

It will be shown below that Eq. (A) is a good approximation.

Table 1 shows that the benzene formation is less than 3% of the products measured at the reduced intensities of the incident light which is favorable for polymerization. Therefore, Reactions 6—9 are neglected in the following kinetic considerations at relatively high intensities.

A steady-state treatment gives the following equation:

$$\frac{[C_2H_2]_{\text{initial}}}{[C_2H_4]_{\text{initial}}} = \frac{k_1}{k_2}[(r_B^*/r_B)^{1/2} - 1], \qquad (1)$$

where r_B* is the rate of the formation of n-butane in Reaction 3 when ethylene is alone, and where r_B is that when acetylene is added to it.

Cvetanović and Doyle[3)] have discussed the case when f is not unity. They have assumed the rate constant of the cross interaction of two radicals to be twice the arithmetic mean of the rates of the self-interaction of the radicals, *i.e.*:

$$k_4 + k_{4a} + k_{4b} = (k_3+k_{3a}) + (k_5+k_{5a}) = (1+f)k. \qquad \text{(B)}$$

This seems to be logical.

Under such conditions, the steady-state treatment gives the following expression for k_2/k_1:

$$\left(\frac{k_2}{k_1}\right)^{*} = \frac{[\mathrm{C_2H_4}]}{[\mathrm{C_2H_2}]}\left\{\left[\delta\left(\frac{r_\mathrm{B}}{r_\mathrm{B}^{*}}\right)^{1/2}\left(1+\frac{(\delta^2-1)r_\mathrm{B}}{r_\mathrm{B}^{*}}\right)^{1/2} - \frac{(\delta^2-1)r_\mathrm{B}}{r_\mathrm{B}^{*}}\right]^{-1}-1\right\}, \qquad \text{(1a)}$$

where $\delta=(1+f)/2f^{1/2}$.

From Eqs. (1) and (1a), it may be seen that:

$$\rho = \frac{(k_2/k_1)^{*}}{k_2/k_1} = \left\{\left[\delta\left(\frac{r_\mathrm{B}}{r_\mathrm{B}^{*}}\right)^{1/2}\left(1+\frac{(\delta^2-1)r_\mathrm{B}}{r_\mathrm{B}^{*}}\right)^{1/2} - \frac{(\delta^2-1)r_\mathrm{B}}{r_\mathrm{B}^{*}}\right]^{-1}-1\right\}\left[\left(\frac{r_\mathrm{B}^{*}}{r_\mathrm{B}}\right)^{1/2}-1\right]^{-1}.$$

They have computed ρ for a wide range of f and $r_\mathrm{B}^*/r_\mathrm{B}$ values and have shown that even when $f=0.6$, ρ differs from unity by less than 2% in the range of $(r_\mathrm{B}^*/r_\mathrm{B})\leq 7$.

In the present case, the rates of the self-interaction of ethyl and vinyl radicals may be almost equal to the collision numbers, so that:

$$f = \frac{k_5+k_{5a}}{k_3+k_{3a}} = \frac{\sigma^2(\mathrm{C_2H_3})}{\sigma^2(\mathrm{C_2H_5})}\left[\frac{M(\mathrm{C_2H_5})}{M(\mathrm{C_2H_3})}\right]^{1/2},$$

where σ and M are the collision cross section and the molecular weight of each radical respectively. The collision diameters are $\sigma(\mathrm{C_2H_3})=4.23$ Å and $\sigma(\mathrm{C_2H_5})=4.33$ Å,[16)] which give 0.989 as the value of f. Therefore, we have used Eq. (1) instead of (1a) to obtain k_1/k_2.

The steady-state treatment for the reaction mechanism described above leads to:

$$\frac{R(\mathrm{C_2H_6})}{R(n\text{-}\mathrm{C_4H_{10}})} = \frac{k_{4a}}{k_4}\cdot\frac{R(1\text{-}\mathrm{C_4H_8})}{R(n\text{-}\mathrm{C_4H_{10}})} + \frac{k_{3a}}{k_3}, \qquad (2)$$

$$\frac{R(\mathrm{C_2H_6})}{R(n\text{-}\mathrm{C_4H_{10}})} - \frac{k_{3a}}{k_3} = \frac{k_{4a}}{k_3}[(r_\mathrm{B}^{*}/r_\mathrm{B})^{1/2}-1], \qquad (3)$$

and

$$\frac{R(1,3\text{-}\mathrm{C_4H_6})}{R(n\text{-}\mathrm{C_4H_{10}})} = \frac{k_5}{k_3}[(r_\mathrm{B}^{*}/r_\mathrm{B})^{1/2}-1]^2. \qquad (4)$$

Taking the data from Table 1, one can plot Eqs. (1)—(4) as is shown in Figs. 1—4. Good linear plots are obtained, as required by the equations. The slope of each figure gives the relative rate constant.

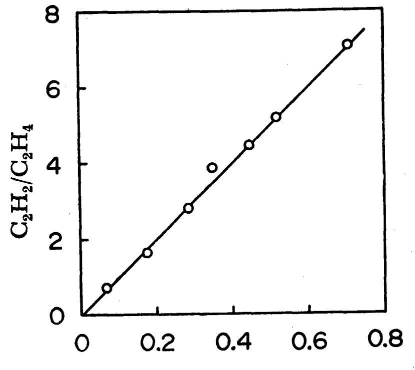

Fig. 1. Experimental plot of Eq. (1).

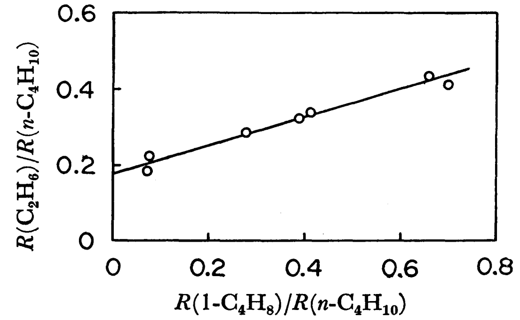

Fig. 2. Experimental plot of Eq. (2).

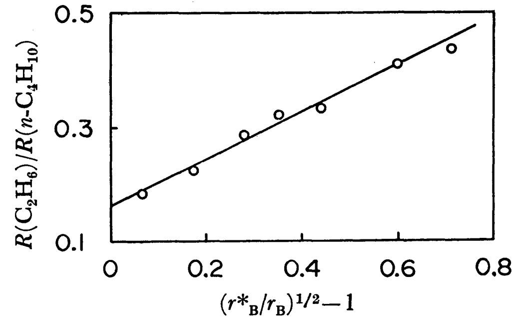

Fig. 3. Experimental plot of Eq. (3).

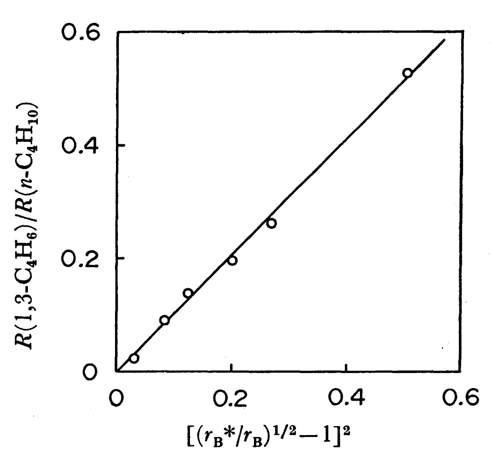

Fig. 4. Experimental plot of Eq. (4).

Using these relative rate constants and Eq. (A), the rate constants of Reactions 3a—5a relative to that of Reaction 3 are calculated to be as is shown in Column 2 of Table 2; they have not been measured hitherto. Column 3 shows the recalculated values expressed in a way similar to the literature values given in the last column.

It can be seen that a good agreement exists between the value of k_1/k_2 obtained in the present work and that of Cowfer, *et al.*[5)] though their value has been obtained at total pressures of 10—15 Torr. However, there are some complications involved in obtaining the absolute value of k_2 from the new relative value for acetylene. The main one is that the rate constant for H-atom addition to ethylene is complicated by the redissociation of the vibrationally excited ethyl radical. Therefore, in the region of low pressures the absolute value of k_1 shows a tendency to increase with an increase in the total pressures.[17)] Recetnly, Eyre *et al.*,[17j)] have obtained the value of k_1

Table 2. Summary of the relative rates of reactions of C_2H_3 and C_2H_5 radicals

Reactions	Relative rate constants			Ref.
	Present results (22.7°C)		Literature values	
1	2	3	4	
$H+C_2H_4 \rightarrow C_2H_5$	9.99±0.16		8.6±1.3	6
$H+C_2H_2 \rightarrow C_2H_3$	1.00		1.00	
$C_2H_5+C_2H_5 \rightarrow n\text{-}C_4H_{10}$	1.00			
$\rightarrow C_2H_6+C_2H_4$	0.157±0.002			
$C_2H_5+C_2H_3 \rightarrow 1\text{-}C_4H_8$	1.13±0.20	1.00	1.00	
$\rightarrow C_2H_6+C_2H_2$	0.417±0.016	0.369	0.115(161—175 °C)	7
$\rightarrow 2C_2H_4$	0.77±0.20	0.68	0.034(161—175 °C)	7
$C_2H_3+C_2H_3 \rightarrow 1,3\text{-}C_4H_6$	1.03±0.04	1.00	1.00	
$\rightarrow C_2H_4+C_2H_2$	0.09±0.04	0.087	0.02(50±0.05 °C)	8
			~0.5(272—301 °C)	9
			1.1(175 °C)	10
			~3	11

Table 3. Absolute rate constant for $H+C_2H_2$

Rate constant cc $mol^{-1}s^{-1}\times10^{10}$	Temp. °C	Pressure Torr
0.78		0.7—2.1(He)$^{a)}$
0.81	17	3.5(H_2)$^{b)}$
2.4±0.3	40	1.35—3.00(Ar)$^{c)}$
2.7±0.7	room temp.	10—15(He)$^{d)}$
3.6	30	0.5—30(He)$^{e)}$
5.2	25	1.0—15(H_2)$^{f)}$
36		3—17.3(He)$^{a)}$
5.5±0.5	22.7	~650(H_2)$^{g)}$

a) Ref. 18. b) J. R. Dingle and D. J. Le Roy, *J. Chem. Phys.*, **18**, 1632 (1950). c) Ref. 19. d) Ref. 6. e) Ref. 5. f) E. L. Tollefson and D. J. Le Roy, *J. Chem. Phys.*, **16**, 1057 (1948). g) This work.

$=(5.5\pm0.5)\times10^{11}$ cm^3 mol^{-1} s^{-1}, independent of H_2 pressures of 750—1750 Torr at 298 K; the pressure region and the temperature are close to those used in the present work. If this absolute value is adopted, the relative rate constant obtained in this work leads to $(5.5\pm0.5)\times10^{10}$ cm^3 mol^{-1} s^{-1} as the rate constant for the addition of the H atom to acetylene; it is tabulated in Table 3. Recent studies[5,6,18–20] have indicated that the value of k_2 shows a pressure dependence when determined in the low-pressure region (1 to 50 Torr). This pressure dependence seems to be the reason for the discrepancies in the absolute values given in Table 3. In order to obtain a more reliable value, it may be necessary to study the decomposition of the vibrationally excited vinyl radicals over a wide range of pressures.

The agreements are not good between the literature values and those obtained in the present work for the ratio of the rate constants for the disproportionation to the combination of vinyl and ethyl radicals. There is uncertainty in the analysis of the data to obtain the ratio, as has been mentioned by authors themselves in their papers;[9,11] moreover, the available data are few in number. However, it can be seen at least that the value obtained for the vinyl radical reaction agrees in the order of magnitude with that proposed by Sherwood and Gunning.[7] Though a detailed discussion is impossible at present, it seems safe to conclude that the rate constant of the disproportionation of the vinyl radical does not exceed that of the recombination by one-tenth at room temperature.

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