

The Reaction of Hydrogen Atoms with Acetylene

D. J. LeRoy and E. W. R. Steacie

Citation: *The Journal of Chemical Physics* **12**, 369 (1944); doi: 10.1063/1.1723959

View online: <http://dx.doi.org/10.1063/1.1723959>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/12/9?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Exchange reactions of atomic hydrogen with acetylene and ethylene](#)

AIP Conf. Proc. **172**, 647 (1988); 10.1063/1.37498

[Reaction of Hydrogen Atoms with Acetylene](#)

J. Chem. Phys. **46**, 4969 (1967); 10.1063/1.1840662

[MassSpectrometric Investigation of the Reactions of Atomic Hydrogen with Acetylene](#)

J. Chem. Phys. **44**, 4010 (1966); 10.1063/1.1726564

[Kinetics of the Reaction of Atomic Hydrogen with Acetylene](#)

J. Chem. Phys. **18**, 1632 (1950); 10.1063/1.1747552

[The Reaction of Atomic Hydrogen with Acetylene](#)

J. Chem. Phys. **16**, 1057 (1948); 10.1063/1.1746724



The fraction associated, x , is $2p_2/p_1$, and $m_2=2m_1$, so that

$$p_1 = \frac{p_m}{1 + (\sqrt{2}/2)x} \quad (\text{A-8})$$

$$\frac{\partial \ln p_1}{\partial(1/T)} = \frac{\partial \ln p_m}{\partial(1/T)} - \frac{\sqrt{2}}{2} \frac{\partial x}{\partial(1/T)} \quad (\text{if } x \text{ is small}) \quad (\text{A-9})$$

$$\Delta H_1 = \Delta H_m + R \frac{\sqrt{2}}{2} \frac{\partial x}{\partial(1/T)}. \quad (\text{A-10})$$

The fraction associated, x , can be shown to obey the equation

$$x = 2p_2/p_1 = 2 \exp \{ [(S_2^0 - S_1^0 - S_c^0)/R] - [(\Delta H_2 - \Delta H_1)/RT] \} \quad (\text{A-11})$$

$$\frac{\partial x}{\partial(1/T)} = -x(\Delta H_2 - \Delta H_1)/R. \quad (\text{A-12})$$

If we insert numerical values in Eqs. (A-10), (A-11), and (A-12), using $x=0.02$ and $S_2^0=114 \pm 6$, we find the error in ΔH_1 to be

$$0 < \left[\frac{\sqrt{2}}{2} x (\Delta H_2 - \Delta H_1) \right] < 0.2 \text{ kcal.} \quad (\text{A-13})$$

If we use $x=0.003$, we find the error to be

$$0 < \left[\frac{\sqrt{2}}{2} x (\Delta H_2 - \Delta H_1) \right] < 0.05 \text{ kcal.} \quad (\text{A-13a})$$

It is interesting to note that we are also able by Eq. (A-11) to set an upper limit on the heat of association (using $x=0.02$):

$$(\text{KCl})_2 \rightarrow 2\text{KCl}, \quad \Delta H < 47 \text{ kcal. (at } 800^\circ\text{K).} \quad (\text{A-14})$$

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 12, NUMBER 9 SEPTEMBER, 1944

The Reaction of Hydrogen Atoms with Acetylene*

D. J. LE ROY† AND E. W. R. STEACIE
National Research Laboratories, Ottawa, Canada

(Received July 13, 1944)

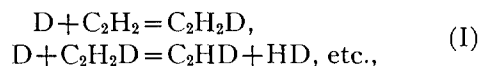
An investigation has been made of the reaction between hydrogen atoms and acetylene. With the large hydrogen atom concentrations produced in the discharge tube, catalytic recombination of hydrogen atoms occurs but no hydrogenated products could be detected. With small hydrogen atom concentrations resulting from mercury photosensitization, ethane and butane are produced together with a partially hydrogenated polymer. The results are discussed from the point of view of the elementary reactions involved and it is concluded that ethyl and vinyl radicals play an important part in the reaction.

INTRODUCTION

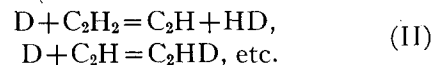
IN a previous paper¹ on the mercury photosensitized polymerization of acetylene it was concluded that hydrogen atoms and C₂H radicals are probably produced in the initial step and that the polymerization is sensitized by these primary products. In an attempt to throw further light on the problem, the present paper is devoted to an investigation of the action of hydrogen atoms on acetylene.

This has already been done by a number of workers who produced hydrogen atoms either by a discharge tube²⁻⁵ or by mercury photosensi-

tization.⁶ In the case of the discharge-tube method it was found that although acetylene catalyzed the recombination of hydrogen atoms, no products other than hydrogen and acetylene could be detected. However, if deuterium atoms were used⁵ deuterization of acetylene took place with an activation energy of less than 5 kcal. In order to explain the rapid exchange as well as atom recombination, Geib and Steacie⁵ suggested the alternative mechanisms



and



* Contribution No. 1214 from the National Research Laboratories, Ottawa, Canada.

† Present address: Department of Chemistry, University of Toronto.

¹ D. J. Le Roy and E. W. R. Steacie, *J. Chem. Phys.* **12**, 117 (1944).

² K. F. Bonhoeffer and P. Harteck, *Zeits. f. physik. Chemie* **139**, 64 (1928).

³ H. v. Wartenberg and G. Schultze, *Zeits. f. physik. Chemie* **B2**, 1 (1929).

⁴ K. H. Geib and P. Harteck, *Ber.* **66**, 1315 (1933).

⁵ K. H. Geib and E. W. R. Steacie, *Zeits. f. physik. Chemie* **B29**, 215 (1935). *Trans. Roy. Soc. (Canada)* **III**, **29**, 91 (1935).

⁶ J. R. Bates and H. S. Taylor, *J. Am. Chem. Soc.* **49**, 2438 (1927).

TABLE I.

Temperature	C ₂ H ₂	H ₂	Time	-ΔP	-ΔH ₂	-ΔC ₂ H ₂	Gaseous products
25°C	22 mm	396 mm	45 min.	— mm	— mm	8.2 mm	1.3 mm
25	22	400	45	15	—	11.4	1.5
25	22	403	45	10	4.0	6.8	0.9
200	22	404	15	19	11	9.8	1.9
200	22	400	15	16.5	11	7.1	1.6
200	22	403	15	20	10	12.2	2.2
200	22	418	15	17	7.5	11.9	2.4
200	22	401	15	15	9	7.6	1.6
300	22	404	15	32	19	18.4	5.4
300	22	403	15	31	19	16.2	4.2
300	22	399	15	25	16	12.2	3.2

In other words, the experimental results could be explained on the assumption that the primary step consisted of the formation of either the vinyl radical or the ethynyl radical. At the present time there is no method of deciding between the two mechanisms.

Bates and Taylor⁶ have reported experiments in which they subjected hydrogen-acetylene mixtures to mercury photosensitization. The reaction appeared to be largely one of polymerization, since they were unable to detect any saturated products. However, their hydrogen pressure was not high enough to prevent appreciable quenching by acetylene so that hydrogenation, if it occurred, was probably masked by a considerable amount of straight polymerization.

Disregarding the work of Bates and Taylor, which was of course largely of an exploratory nature, we are left with the problem of trying to explain the absence of hydrogenation in the presence of hydrogen or deuterium atoms. It consequently seemed desirable to re-investigate not only the mercury photosensitized hydrogenation but also the reaction of hydrogen atoms produced in a discharge tube, in the hope that it might be possible to find hydrogenated products which had previously escaped detection.

A. HYDROGEN ATOMS PRODUCED IN THE DISCHARGE TUBE

The discharge tube was of the usual type and was operated by a 5000-volt 2½-kva transformer. Using a hydrogen flow rate of 75 cc per min. at atmospheric pressure and an operating pressure of 0.4 mm the contact time was 0.5 sec. A Wrede gauge⁷ indicated an atom concentration of ap-

proximately 35 percent. Acetylene could be admitted to the reaction vessel at either 6.5 or 1.6 cc (at atmospheric pressure) per min. The procedure was to start with an accurately determined volume of acetylene and transfer it to a vessel where it could be admitted to the reaction vessel at a constant rate by raising a mercury levelling bulb. When most of the acetylene had been brought into the hydrogen atom stream in this way, the discharge was stopped and the remaining acetylene pumped through the apparatus and combined with the products.

To avoid loss of any ethane or ethylene which might be produced, the products were not condensed in the usual way, but after passing through the four-stage mercury diffusion pump they were condensed in a trap filled with silica gel and cooled with liquid air. The hydrogen which passed through this trap was pumped off by a Megavac pump. Steacie and Phillips⁸ used silica gel in this way and found that they could separate methane from hydrogen with high efficiency.

The catalysis of the recombination of hydrogen atoms by acetylene was investigated by inserting two adjacent thermocouple wells in the lower part of the reaction vessel. One of these was poisoned, as was the rest of the apparatus, by phosphoric acid. The other was wound with a few turns of silver wire and, by measuring the difference in temperature between the two wells, it was possible to get an indication of the hydrogen atom concentration from the rate of recombination on the silver wire. On admitting acetylene the temperature immediately began to fall and the rate of temperature decrease for a given temperature was the same as it was for the discharge shut off, i.e., for no atoms present, indicating complete removal of hydrogen atoms in the presence of acetylene.

The volume of gaseous products collected at the end of a run was found to agree with that originally taken within about one percent and chemical analysis showed no gas other than acetylene. It would appear, then, that although acetylene will catalyze the recombination of hydrogen atoms and be almost completely deuterized if deuterium atoms are used,⁵ no hydrogenation occurs under these conditions.

⁷ E. Wrede, *Zeits. f. Instrumentenk.* **48**, 201 (1928); P. Harteck, *Zeits. f. Physik. Chemie* **A139**, 98 (1928).

⁸ E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.* **4**, 461 (1936).

TABLE II.

C_2H_2	H_2	Time	$-\Delta P$	25°C				
				$-\Delta H_2$	$-\Delta C_2H_2$	" C_2H_4 "	C_2H_6	C_4H_{10}
0.35 mm	4.28 mm	22 min.	0.13 mm	0.098 mm	0.057 mm	0.003 mm	0.018 mm	0.002 mm
0.37	4.15	45	.24	.182	.126	.004	.031	.012
0.36	4.07	120	.48	.307	.267	.004	.057	.025

B. HYDROGEN ATOMS PRODUCED BY MERCURY PHOTSENSITIZATION

The first series of runs was done using a quartz annular cell and the full radiation of the lamp.⁹ The results are shown in Table I.

Column one gives the temperature; two, the original pressure of acetylene; three, the original pressure of hydrogen; four, the duration of the run; five, the observed pressure decrease; six, the amount of hydrogen used up expressed in mm; seven, the amount of acetylene used up also in mm; and eight, the amount of gaseous products formed.

The observed pressure decreases at 300°C exceed the initial pressure of acetylene, indicating

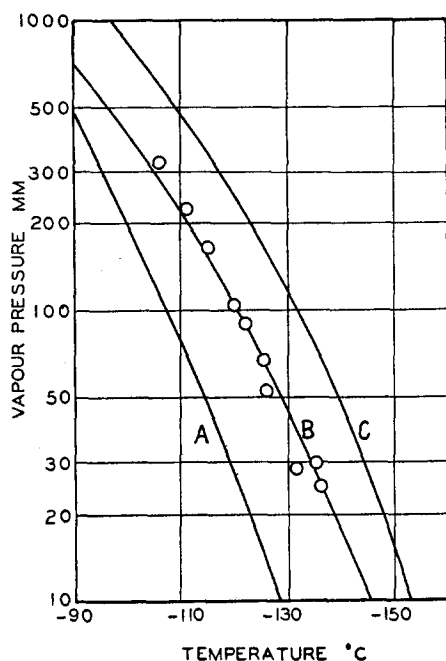


FIG. 1. The circles represent the vapor pressure of gaseous products from two runs at 25°C. The solid lines A, B, and C are for acetylene, ethane, and ethylene, respectively.

⁹ D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.* **10**, 676 (1942).

that considerable hydrogenation took place. This was also observed at room temperature when runs of long duration were made. It is also apparent from the table that the rate of hydrogenation increased considerably with temperature.

Analysis of the gaseous products offered some difficulty owing to their small volume. Acetylene was removed from the condensible products at the end of a run by shaking with potassium mercuric iodide. The remaining gas was collected, freed from water vapor, and measured. Its vapor pressure was then determined over a range of temperature by the method of Benson.¹⁰ The results are shown in Fig. 1. The solid lines A, B, and C give the vapor pressures of pure acetylene, ethane, and ethylene, respectively. The experimental points are for two separate runs at 25°C and indicate that ethane is an important product. Further evidence in this regard is given below.

A second series of runs was made at a total pressure of about 4.5 mm and 25°C using the system previously described (Series I, reference 1). The results are given in Table II.

The first six column headings have the same significance as in Table I but in this case a more complete analysis of the gaseous products was made. After removing the hydrogen the condensible gas was collected and analyzed by means of the Blacet-Leighton apparatus.¹¹

The decrease in hydrogen was calculated from the observed pressure decrease together with the volume of condensible gas. The latter was measured by compressing it into a calibrated volume by means of a mercury diffusion pump backed by a Toepler pump. It was then transferred to the gas analysis apparatus with a diffusion pump backed by an automatic Sprengel pump. Acetylene was absorbed with a potassium hydroxide-

¹⁰ S. W. Benson, *Ind. Eng. Chem. Anal. Ed.* **14**, 189 (1942).

¹¹ F. E. Blacet and P. A. Leighton, *Ind. Eng. Chem. Anal. Ed.* **3**, 266 (1931).

mercuric cyanide bead, and ethylene with fuming sulphuric acid. The residue was analyzed by combustion and the carbon and hydrogen values agreed best on the assumption that this gas was a mixture of ethane and butane. The amounts of these products, expressed in mm, are given in the last two columns of Table II. There was such a small amount of unsaturated gas in the mixture after removing the acetylene that accurate analysis was precluded. Consequently it was merely called " C_2H_4 " although there is a possibility that it was a higher olefin or even a small amount of paraffin which dissolved in the fuming sulphuric acid. The amount of this substance is given in column seven. With the exception of this " C_2H_4 " the values for the other products are quite reliable because the small amount of gas needed for an analysis made it possible to do several determinations on the products of a given run.

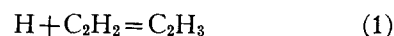
The results of the two series are then in reasonably good agreement and point to ethane as an important product. In the latter series carbon and hydrogen balances were made on the over-all reaction and they indicated that the acetylene disappearing by processes other than the formation of "ethylene," ethane, and butane was equivalent to slightly more than the amount used up in forming these products. The empirical formula of the polymer was approximately $(C_2H_4)_x$.

It is unfortunate that " C_2H_4 " was produced in such a small percentage because, while ethane and butane formation increased continuously with time, " C_2H_4 " appeared to reach a constant value of 0.004 mm. This might be taken to indicate that " C_2H_4 " is an intermediate in the formation of ethane and butane but the evidence is not very reliable.

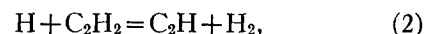
DISCUSSION

The important point about this work is that while no hydrogenation occurs with the high hydrogen atom concentrations of the discharge tube it takes place readily at the low concentrations resulting from mercury photosensitization. Regardless of whether mechanism I or II of Geib and Steacie is correct it would seem to be necessary that vinyl radicals be formed before any

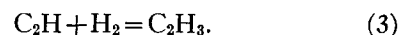
hydrogenation can take place. This could occur by either



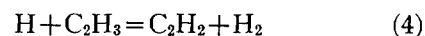
or



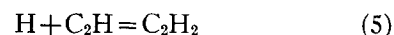
followed by



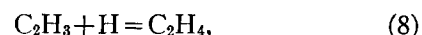
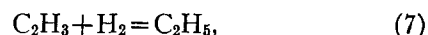
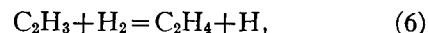
The absence of hydrogenation in the discharge-tube method could then be explained on the assumption that the reaction



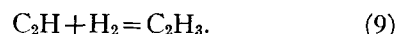
or



occurs much more readily in the presence of high hydrogen atom concentrations than the reactions

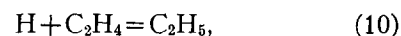


and

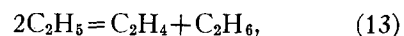
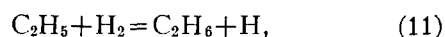


It is difficult to see how (8) would occur in the photosensitized experiments and not with the discharge tube unless it involved a ternary collision. And since the total pressure in the discharge-tube method was just about one-tenth of the lower pressure used in the former method, it would seem likely that (8) is not involved at all, even as a ternary reaction.

If ethylene actually is an intermediate the most likely method of formation is (6). Ethane and butane formation would then involve (10):



which is known to have a small activation energy. Whether this is followed by



is open to question but it is known that butane is formed at room temperature in systems containing hydrogen, ethylene, and acetylene¹² and

¹² D. J. Le Roy and E. W. R. Steacie, *J. Chem. Phys.* **9**, 829 (1941).

both (12) and (13) are generally conceded to have small activation energies.¹³

If ethylene is not a true intermediate the gaseous products could be accounted for by the reactions (7), (11), (12), and (13).

Polymer formation is undoubtedly sensitized by radicals for even if the mercury photosensitized polymerization in the absence of hydrogen¹ were not a free radical process, the large H₂:C₂H₂ ratios used in this work would largely eliminate the possibility of quenching Hg(³P₁) atoms by acetylene. Furthermore, Jungers and Joris¹⁴ have shown that ethyl radicals will sensitize the polymerization of acetylene and while there is little direct evidence for a sensitized polymerization by vinyl radicals, the analogous reaction with ethylene has been fairly well established.^{9,15,16}

¹³ *Annual Tables of Physical Constants* (1942), Section 602.

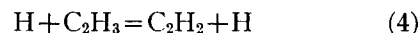
¹⁴ J. C. Jungers and G. G. Joris, *Bull. Soc. Chim. Belg.* **50**, 61 (1941).

¹⁵ E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.* **10**, 22 (1942).

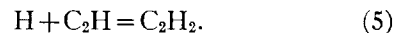
¹⁶ H. Habeeb, D. J. LeRoy, and E. W. R. Steacie, *J. Chem. Phys.* **10**, 261 (1942).

The main points in connection with the reaction between hydrogen atoms and acetylene can be summarized as follows:

(1) With high hydrogen atom concentrations hydrogenation of acetylene is prevented by



or



(2) With low hydrogen atom concentrations hydrogenation does occur, with the formation of ethane and butane.

(3) The hydrogenated products can best be accounted for on the assumption that both vinyl and ethyl radicals are formed.

(4) A partially hydrogenated polymer is formed as the result of a radical sensitized polymerization of acetylene.

(5) The results lend some weight to the assumption that the mercury photosensitized polymerization of acetylene proceeds by a free radical process.