

The Mercury (3 P 1) PhotoSensitized Hydrogenation of Ethylene

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The Mercury (3P_1) Photo-Sensitized Hydrogenation of Ethylene

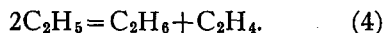
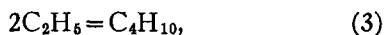
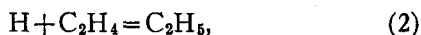
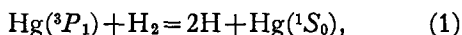
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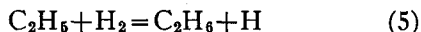
(Received August 1, 1947)

The mercury photo-sensitized hydrogenation of ethylene has been investigated over the temperature range 42°C to 320°C. At 200°C and lower, the results are in relatively close agreement with those of Jungers and Taylor. The activation energy of the reaction, $2C_2H_5 = C_2H_6 + C_2H_4$, is estimated to be ≥ 1.2 kcal. per mole. Above 200°C ethane formation increases rapidly, corresponding to an activation energy ≥ 10.5 kcal. per mole for the reaction $C_2H_6 + H_2 = C_2H_8 + H$. The small amount of polymerization was not affected by temperature.

THE mercury photo-sensitized reaction between hydrogen and ethylene has been investigated by a number of workers,¹ but not over a wide range of temperature. Jungers and Taylor² and Moore and Taylor³ made a careful study of the reaction at room temperature and postulated the following mechanism:



The only products reported by Moore and Taylor were methane, ethane and butane, in the ratio 2:14:84. Ethane formation by the reaction



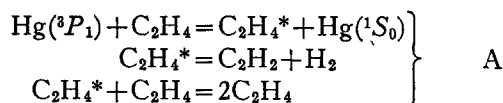
was discounted on the basis of an estimated activation energy greater than 11 kcal. per mole. This number was assumed by analogy with the corresponding reaction with methyl radicals.⁴ Reaction (5) would be expected to occur with an appreciable rate at higher temperatures, and this has been confirmed by us. Trenner, Morikawa, and Taylor⁴ found considerable deuteration of ethane above 100°C in the reaction of atomic deuterium with ethane and attributed

this to the reaction

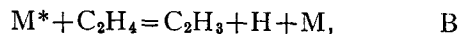


Assuming a steric factor of 0.1, they estimated the activation energy of this reaction to be 11.4 kcal. per mole (110°C). It would seem likely, however, that the exchange takes place by reaction (5).

The present investigation was originally undertaken in an attempt to clarify certain points in connection with the mercury photo-sensitized reaction of ethylene. At room temperature the formation of the initial products, hydrogen and acetylene, is in agreement with the following mechanism:⁵



The reaction is not inhibited by nitric oxide⁶ and the excited ethylene molecules can be deactivated by collisions with carbon dioxide⁷ as well as with ethylene molecules. At high temperatures⁸ the rapid initial pressure decrease is eliminated by nitric oxide, giving rise to a reaction identical with that at room temperature. The high temperature reaction is similar in many respects to the photosensitized reactions in which $Cd(^1P_1)$ and $Zn(^1P_1)$ atoms are used, and for which the alternative primary step,



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¹ W. A. Noyes and P. A. Leighton, *The Photochemistry of Gases* (Reinhold Publishing Corporation, New York, 1941).

² J. C. Jungers and H. S. Taylor, *J. Chem. Phys.* **6**, 325 (1938).

³ W. J. Moore and H. S. Taylor, *J. Chem. Phys.* **8**, 504 (1940).

⁴ N. R. Trenner, K. Morikawa and H. S. Taylor, *J. Chem. Phys.* **5**, 203 (1937).

⁵ D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.* **9**, 829 (1941).

⁶ D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.* **10**, 676 (1942).

⁷ Daphne Line and D. J. LeRoy, *J. Chem. Phys.* **13**, 307 (1945).

was assumed.^{8,9} Since it is unlikely that the primary process, B, would have a large temperature coefficient, it was assumed that the marked effect of temperature was due to the free radical sensitized polymerization of ethylene. We have, accordingly, undertaken an investigation of the polymerization of ethylene initiated by hydrogen atoms and vinyl radicals; the results for atomic hydrogen are given in this report.

EXPERIMENTAL DETAILS

The reaction vessel was a fused quartz annular cell 9 inches long, having a 4-inch external diameter and a 2-inch internal diameter, and connected to the rest of the system by two quartz-to-pyrex graded seals. The gases were saturated with mercury vapor by continuous circulation over mercury dispersed throughout a trap which was maintained at room temperature. The circulating pump was of the constant pressure type referred to previously.⁶ Pressures were read on a wide-bore U-tube manometer.

The three lamps used during the course of the investigation were of the low pressure, mercury-argon type and were operated by a 3000-volt, 60-ma Jefferson transformer. The central portion of the lamp was of quartz and when in use it was inserted through the hole in the annular cell, with the electrode chambers well outside the furnace. It was found that with this arrangement the light intensity is practically independent of the temperature of the furnace. At high temperatures, the natural blue color of the discharge did not appear until about ten minutes after turning on the current, but its appearance was quite sudden and coincided with the initiation of the reaction. In most experiments, the lamp was surrounded by a thin cylindrical glass tube to reduce the light intensity; this tube is referred to as the filter.

The ethylene was obtained from the Ohio Chemical and Manufacturing Company and was said to be 99.5 percent pure. It was further purified and freed from air by a series of bulb-to-bulb distillations. The middle fraction was stored in a 2-liter bulb, isolated from the rest of the

TABLE I. Reaction products at 42°C. All measurements are in mm of mercury at 25°C.

Lamp	Time (min.)	C_2H_4	H_2	$-\Delta P$	CH_4	C_2H_6	C_3H_8	C_4H_{10}	$>C_4H_{10}$
No. 2— no filter	12	12.2	113.8	11.2	0.51	2.1 ₁	0.2 ₁	3.6	0.2
	12	12.4	358.8	11.1	0.3	1.7 ₁	0.4 ₁	3.9 ₁	0.1 ₁
No. 3— with filter	180	15.7	105.1	10.4	0.1	0.9 ₁	0.2 ₁	4.1 ₁	0.1 ₁
	180	15.7	309.6	9.8	0.1	1.1 ₁	—	4.0 ₁	0.0 ₁

system by a mercury cut-off. Hydrogen was purified as required by passing the commercial electrolytic gas through platinized asbestos at 500°C and then through two traps cooled with liquid air, the second containing silica gel. Before using the silica gel trap it was found that 0.3 percent of the gas would not diffuse through a warm palladium tube; with its use this was reduced to 0.02 percent. The ethane, propane, normal butane and acetylene used to calibrate the analytical apparatus were purified in the same manner as the ethylene.

The course of the reaction was followed both by pressure changes and by chemical analyses. At the end of an experiment, the system was opened to a trap cooled with liquid air and allowed to stand for 40 minutes. Most of the condensable gas was frozen out in this way. This trap was then opened to a second one containing silica gel and also cooled with liquid air. After 15 minutes the hydrogen was pumped off slowly until the pressure in the system had fallen to 10^{-3} mm. The traps were then isolated from each other and from the system. The first contained most of the higher hydrocarbons; the second contained methane, some residual hydrogen and a small amount of higher hydrocarbons. The gas in the first trap was transferred to a low temperature fractionating column where it was

TABLE II. Reaction products at higher temperatures. All measurements are in mm of mercury at 25°C. Lamp No. 3, with filter.

Temp.	C_2H_4	H_2	$-\Delta P$	CH_4	C_2H_6	C_3H_8	C_4H_{10}	$>C_4H_{10}$
200°C	14.9	99.7	5.3	0.0 ₁	0.6 ₁	0.0 ₁	1.3 ₁	0.3 ₁
200	14.8	278.0	5.5	0.0 ₁	0.6 ₁	0.0 ₁	1.3 ₁	0.2 ₁
260	14.7	96.8	7.2	0.0 ₁	1.5 ₁	0.1 ₁	1.7 ₁	0.5 ₁
260	14.2	182.0	7.6	0.0 ₁	1.5 ₁	0.2 ₁	1.7 ₁	0.4 ₁
260	14.9	274.4	8.9	0.0 ₁	2.4 ₁	0.1 ₁	1.8 ₁	0.5 ₁
280	15.1	92.5	6.4	0.0 ₁	1.1 ₁	0.2 ₁	1.7 ₁	0.4 ₁
280	15.5	176.5	8.0	0.1 ₁	2.5 ₁	0.1 ₁	2.0 ₁	0.3 ₁
280	15.6	280.5	10.0	0.1 ₁	4.1 ₁	0.1 ₁	1.9 ₁	0.4 ₁
300	15.5	92.0	7.3	0.1 ₁	2.1 ₁	0.4 ₁	1.5 ₁	0.4 ₁
300	14.8	176.3	9.5	0.2 ₁	4.5 ₁	0.2 ₁	2.0 ₁	0.4 ₁
300	15.4	289.0	12.7	0.2 ₁	7.1 ₁	0.2 ₁	1.9 ₁	0.3 ₁
320	18.5	89.5	7.7	0.2 ₁	2.5 ₁	0.4 ₁	1.8 ₁	0.4 ₁
320	21.0	279.0	15.5	0.4 ₁	9.5 ₁	0.2 ₁	2.5 ₁	0.4 ₁

⁸ E. W. R. Steacie and D. J. LeRoy, J. Chem. Phys. 10, 22 (1942).

⁹ H. Habeeb, D. J. LeRoy, and E. W. R. Steacie, J. Chem. Phys. 10, 261 (1942).

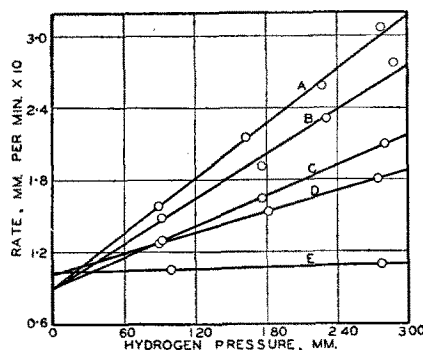


FIG. 1. Effect of hydrogen pressure on the rate of pressure decrease. A, 320°C; B, 300°C; C, 280°C; D, 260°C; E, 200°C.

separated according to carbon number by a method similar to that used by Ward.¹⁰ Blank determinations with known samples showed this procedure to be satisfactory. The various fractions were collected and measured and their olefin content determined.¹¹ The C₂ fractions were tested for acetylene¹² but none was ever found. The hydrocarbons in the silica gel trap were analysed in the same way. The methane and residual hydrogen were collected first and the methane determined by allowing the hydrogen to diffuse through a warm palladium tube on the top of a Toepler pump. The methane analysis was confirmed by combustion, using the Blacet-Leighton apparatus.

The analytical results were expressed in terms of mm of mercury in the reaction system at 25°C. The observed pressures were also converted to the corresponding values at 25°C. This involved an empirical determination of the apparent volume of the system as a function of the furnace temperature.

EXPERIMENTAL RESULTS

Low Temperature

The data for four of the experiments at 42°C are given in Table I. The products are all saturated. Ethane and butane are the main products, and their ratio appears to depend on

¹⁰ E. C. Ward, *Ind. Eng. Chem. Anal. Ed.* 10, 169 (1938).
¹¹ Rowena Pyke, Allan Kahn and D. J. LeRoy, *Ind. Eng. Chem. Anal. Ed.* 19, 65 (1947).

¹² F. E. Blacet, A. L. Sellers and W. J. Blaedel, *Ind. Eng. Chem. Anal. Ed.* 12, 356 (1940).

the light intensity. The relatively small amount of methane, propane and higher paraffins precludes any conclusion as to the effect of light intensity on their production. In both groups of experiments it is apparent that the rates are independent of hydrogen pressure. In a series of experiments of increasing duration and in which the filter was used, it was found that both ethane and butane formation are linear in time until over 80 percent of the ethylene is used up, indicating that the rates are also independent of ethylene pressure. With the exception of the effect of light intensity, these results are in essential agreement with the work of Taylor *et al.*

Higher Temperatures

The results of a series of experiments covering the range 200°C to 320°C are given in Table II. Blank experiments without illumination showed no evidence of a thermal reaction. Each experiment lasted approximately 50 minutes. As in the case of the low temperature experiments, the products are all saturated and the rate of pressure decrease remained constant throughout any one experiment. The rate of formation of methane and propane would appear to increase with temperature; a plot of one against the other points to a methane: propane ratio nearer to 2:1 than to 1:1. The rate of formation of butane and higher paraffins is relatively insensitive to hydrogen pressure and temperature; ethane production is strongly affected by both these factors.

DISCUSSION OF RESULTS

Our results can be interpreted on the basis of reactions (1) to (5). The rate equations are:

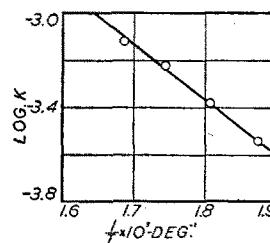


FIG. 2. Log₁₀ of the slopes of curves A, B, C and D (Fig. 1) vs. the reciprocal of the absolute temperature. (Notation below the figure should read $\frac{1}{T} \times 10^3 - \text{DEG.}^{-1}$)

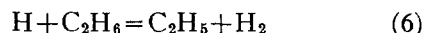
$$\begin{aligned}
 -d[\text{C}_2\text{H}_4]/dt &= 2I_a \left(1 - \frac{k_4}{2(k_3 + k_4)} \right) \\
 &\quad + k_6 \left(\frac{I_a}{k_3 + k_4} \right)^{\frac{1}{2}} [\text{H}_2], \\
 d[\text{C}_2\text{H}_6]/dt &= \frac{k_4 I_a}{k_3 + k_4} + k_5 \left(\frac{I_a}{k_3 + k_4} \right)^{\frac{1}{2}} [\text{H}_2], \\
 d[\text{C}_4\text{H}_{10}]/dt &= \frac{k_3 I_a}{k_3 + k_4}.
 \end{aligned}$$

Since all the products are saturated, the rate of disappearance of ethylene is equal to the rate of pressure decrease. The effect of hydrogen pressure and temperature on the rate of pressure decrease is shown graphically in Fig. 1. The logarithms of the slopes of these curves are plotted against the reciprocal of the absolute temperature in Fig. 2. The corresponding "activation energy," E' , is 10.5 kcal. per mole.

Under conditions where the rate is independent of the hydrogen pressure (i.e. $\leq 200^\circ\text{C}$) the ethane:butane ratio is equal to k_4/k_3 . The experimental ratio, with the filter, at 42°C and 200°C leads to the value $E_4 - E_3 = 1.2$ kcal. per mole. If E_3 can be assumed to be zero¹³ the term $(k_3 + k_4)$ in the slopes of Fig. 1 can be written in the form $k_3[1 + n \cdot \exp(-E_4/RT)]$, where n is equal to unity if the pre-exponential factors of the two rate constants are equal. By plotting the logarithms of $[1 + n \cdot \exp(-E_4/RT)]$ vs. $1/T$ for various values of n it is seen that the "activation energy," E'' , of $(k_3 + k_4)$ is $\leq E_4$. For example, if E_4 is 1.2 kcal. and n is equal to unity then E'' is approximately equal to 0.16 kcal. The activation energy of reaction (5) is equal to $E' + \frac{1}{2}E''$, and hence $10.5 \leq E_5 \leq 11.1$. Regardless of the assumptions made about E_3 and E_4 , $E_5 \geq 10.5$ kcal. per mole. It should be noted that the effect of temperature on the

intercepts of Fig. 1 is in agreement with the fact that $E_4 > E_3$.

The C-H bond strength in ethane¹⁴ has been estimated to be 98 kcal. by Kistiakowski, 97.5 by Polanyi and 96.8 by Stevenson. Since the H-H bond strength is 103.7 kcal., the value of ΔH for reaction (5) is 5.7, 6.2 or 6.9 kcal. The activation energy of the reverse reaction,



would then be in the range 3.6 to 5.4 kcal. per mole, somewhat lower than previous estimates.¹⁴ Since the formation of products other than butane and ethane is not sensitive to temperature, a more elaborate mechanism than the one given would not increase E_5 (and hence E_6) appreciably. Most estimates of E_6 have been based on collision yields, assuming a steric factor of 0.1, and consequently, the solution of the problem will be contingent on future measurements in which an unequivocal value of E_6 is obtained.

There are not sufficient data to interpret the effect of light intensity on the ethane:butane ratio at low temperatures, but it is hoped that experiments now being planned will enable some conclusions to be made regarding light intensity and surface reactions.

It is clear from our work that the polymerization of ethylene sensitized by atomic hydrogen is relatively unimportant. This is surprising in view of the low activation energies assigned to reactions of the type $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 = \text{C}_4\text{H}_9$.¹³

It is a pleasure to acknowledge the financial assistance received from the National Research Council of Canada, which enabled this research to be carried on. The junior author would also like to express his appreciation of the National Research Council Studentship which he held during the year 1946-47.

¹³ Annual Tables of Physical Constants, Section 602.

¹⁴ E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946).