The Mercury Photosensitized Reactions of Ethylene at High Temperatures

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

Articles you may be interested in

---

of the toluene and paracresol spectra that there is more tendency towards photo-decomposition in tyrosine than in phenylalanine.

The spectra of phenylalanine and of tyrosine beyond 2500A are continuous. They consist of more than one absorption system. About 2200A there is expected another absorption of the ring which corresponds to the benzene absorption at 2000A. Furthermore, the "end absorption" of all amino acids irrespective of an aromatic nucleus begins below 2500A and is attributed to the amino group. Due to overlapping it will probably not be possible to separate these different absorptions.
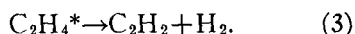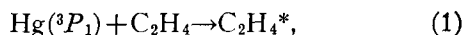

The Mercury Photosensitized Reactions of Ethylene at High Temperatures*

D. J. LeROY AND E. W. R. STEACIE
National Research Laboratories, Ottawa, Canada
(Received August 10, 1942)

The mercury ($^3P_1$) photosensitized reactions of ethylene have been investigated over the temperature range 25°C to 350°C. In addition to those previously found at 25°C, the reaction $Hg(^3P_1)+C_2H_4=C_2H_3+H+Hg(^1S_0)$ is shown to occur. There was a considerable increase in the quantum yield at high temperatures and this is attributed to the hydrogen atom and vinyl radical sensitized polymerization of ethylene. The reactions of ethylene with $Na(^2P)$, $Cd(^3P_1)$, $Zn(^3P_1)$, $Hg(^3P_1)$, $Cd(^1P_1)$, and $Zn(^1P_1)$ atoms are summarized and the latter three are shown to be closely related.

INTRODUCTION

IN a number of recent papers it has been established with considerable certainty that in the mercury ($^3P_1$) and cadmium ($^3P_1$) photosensitized reactions of ethane[1-3] and propane[4, 5] the initial step consists in the removal of a hydrogen atom with the production of the corresponding alkyl radical. In contrast with this behavior of the paraffins, that of ethylene is much more complex. The mercury photosensitized reactions of ethylene[6] have been shown to involve the steps

$$Hg(^3P_1)+C_2H_4 \rightarrow C_2H_4^*, \qquad (1)$$

$$C_2H_4^*+C_2H_4 \rightarrow 2C_2H_4, \qquad (2)$$

$$C_2H_4^* \rightarrow C_2H_2+H_2. \qquad (3)$$

On the other hand, the initial step in the cadmium ($^1P_1$)[7] and zinc ($^1P_1$)[8] photosensitized reactions of ethylene is probably the removal of a hydrogen atom with the formation of a vinyl radical, although the simultaneous occurrence of reactions analogous to those with mercury ($^3P_1$) is not excluded.

Such differences were not unexpected in view of the energies involved. The latest estimates of the C−H bond strength in ethane[9-11] are in the neighborhood of 96 to 98 kcal. while that of propane[9] is 95.5 or 91 kcal. depending on whether the H is removed from a primary or a secondary carbon atom. This makes it possible for a $Hg(^3P_1)$ atom (112.2 kcal.) to remove a hydrogen atom even if the hydride ($\Delta H = 8.5$ kcal.) is not formed and for a $Cd(^3P_1)$ atom (87.3 kcal.) to remove one provided the hydride ($\Delta H = 15.5$ kcal.) is formed. On the other hand, while the C−H bond strength in ethylene is not known

* Contribution No. 1079 from the National Research Laboratories, Ottawa, Canada.
[1] E. W. R. Steacie and N. W. F. Phillips, Can. J. Research **B16**, 303 (1938).
[2] E. W. R. Steacie and R. L. Cunningham, J. Chem. Phys. **8**, 800 (1940).
[3] E. W. R. Steacie and R. Potvin, J. Chem. Phys. **7**, 782 (1939).
[4] E. W. R. Steacie and D. J. Dewar, J. Chem. Phys. **8**, 571 (1940).
[5] E. W. R. Steacie, D. J. LeRoy, and R. Potvin, J. Chem. Phys. **9**, 306 (1941).
[6] D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. **9**, 829 (1941).

[7] E. W. R. Steacie and D. J. LeRoy, J. Chem. Phys. **10**, 22 (1942).
[8] H. Habeeb, D. J. LeRoy, and E. W. R. Steacie, J. Chem. Phys. **10**, 261 (1942).
[9] E. C. Baughan, M. G. Evans, and M. Polanyi, Trans. Faraday Soc. **37**, 377 (1941).
[10] D. P. Stevenson, J. Chem. Phys. **10**, 291 (1942).
[11] H. G. Andersen, G. B. Kistiakowsky, and E. R. Van Artsdalen, J. Chem. Phys. **10**, 305 (1942).

with any certainty, it is probably somewhat greater than that in ethane. The fact that neither $Cd(^3P_1)$ nor $Zn(^3P_1)$ atoms (92.5 kcal.) are able to break the $C-H$ bond in ethylene efficiently and that reaction between ethylene and $Hg(^3P_1)$ atoms is largely (1)–(3) while that with $Cd(^1P_1)$ atoms is probably

$$Cd(^1P_1)+C_2H_4 \rightarrow C_2H_3+H+Cd \text{ (or CdH)},$$
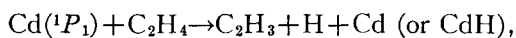
seems to indicate that the $C-H$ bond strength is between 112.2 and 139.9 kcal. There is one difference, however, in the latter two cases. The mercury reaction was investigated at 25°C while the cadmium as well as the zinc reactions were done in the neighborhood of 300°C. This fact led us to the decision to investigate the mercury reaction over a range of temperatures and as we will show below the results more than justified the effort.

EXPERIMENTAL PROCEDURE

Two different types of apparatus were used, the first in which accurate pressure readings were taken and the second in which the products were investigated.

In the first case the reaction vessel consisted of a fused quartz annular cell 12 cm long, 9 cm in diameter with a 5.5-cm diameter hole through the middle. It was mounted in the center of a tubular furnace 90 cm long and 30-cm external diameter. The lamp was inserted through the middle of the cell. A quartz window 3 cm in diameter in the center of the furnace made it possible to examine the lamp without removing it from the furnace. A small trap containing mercury was connected to each end of the reaction vessel just outside the furnace. The mercury in the traps was maintained at room temperature. The gas was kept saturated with mercury vapor by passing it back and forth over the mercury surface in these traps. This was done by raising and lowering two small bulbs containing mercury. Since the bulbs were joined at the bottom the volume of the system was kept constant thus permitting accurate pressure readings to be made during a run. The pressures were read on a wide bore U-tube manometer using the same technique described previously.[6] The total volume of this system was approximately 670 cc, most of which was in the furnace.

In order to make certain that no $Hg(^1P_1)$ atoms were present due to the fused quartz transmitting 1849A, a few runs were made with a thin Pyrex filter between the lamp and reaction vessel. A Pyrex tube approximately 30-mm O.D. was thickened over a distance of a few mm and drawn out and blown simultaneously resulting in a thin portion about 30 mm long and of approximately the same diameter as the rest of the tube. Since the transmission of 2537A was cut down by a factor of approximately 30 it is highly improbable that any light of wave-length 1849A was transmitted.

In the other static runs the light intensity was cut down by a factor of about 20 by inserting a slotted brass tube between the lamp and reaction vessel. The slots extended half way around the diameter of the tube and alternated on the different sides. The number of slots per inch was varied till a suitable rate of pressure change was obtained, permitting accurate readings spread over about three quarters of an hour.

The lamp was of the low pressure type used previously and consisted of a straight tube 100 cm long with an electrode chamber on each end. The central part was of quartz with graded seals connecting to Pyrex. The over-all length was 120 cm, thus permitting the electrode chambers to be outside the furnace. To keep the mercury vapor pressure in the lamp at approximately 2×10^{-3} mm a short tube fastened to the main tube projected downwards and contained mercury. This tube was always kept at room temperature. Tests made with an F.J. 405 photo-tube showed that the light intensity was practically the same at 300°C as at 25°C.

In the apparatus used to determine products, the lamp, reaction vessel, and furnace were the same as that described above with the exception that the slotted brass tube was removed and the full radiation of the lamp used. The remainder of the apparatus was the same as the circulating system described previously.[6] The total volume of this system was approximately 3500 cc. The non-condensible gas was isolated by passing the products through a trap cooled to approximately -200°C. This temperature was obtained by pumping down the liquid air in the vacuum flask surrounding the trap by means of a Hyvac. The volume of non-condensible gas was measured by
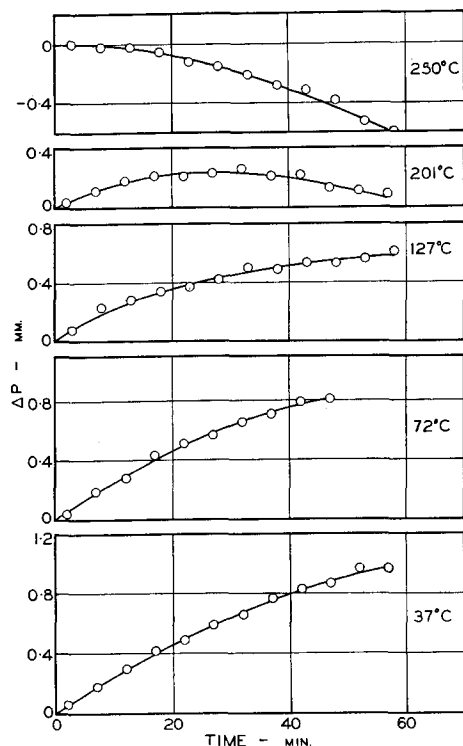
FIG. 1. Pressure change *vs.* time. Initial pressure 15 mm.

compressing it into a calibrated volume by means of a small mercury diffusion pump backed by a Toepler pump. The method of analysis of this gas as well as that of the other products has already been described.[6] The non-condensible gas was found to be entirely hydrogen.

The ethylene used in these experiments was purified in the same manner as before. Nitric oxide was prepared by the reaction of mercury on a two percent solution of sodium nitrite in concentrated sulphuric acid. It was passed through a trap containing a dry ice-acetone mixture and further purified by a bulb-to-bulb distillation using liquid air. Since it was found that ethylene-nitric oxide mixtures reacted slowly at room temperatures forming a deposit on the walls of the storage vessel, these mixtures were made up immediately before they were used.

RESULTS

In Fig. 1 the pressure changes for a series of runs at 15-mm pressure are shown. These results are in sharp contrast to Melville's statement[12]

---

[12] H. W. Melville, Trans. Faraday Soc. **32**, 258 (1936).

that temperature has no effect on the reaction. The initial rate of pressure increase decreases as the temperature is raised till at 250°C the initial pressure rise has disappeared altogether. The possibility that this difference might be due to some $Hg(^1P_1)$ atoms being present was discounted when it was found that runs in which the thin Pyrex filter was used showed the same effect. Furthermore, the relative rates at 25°C and at 300°C were the same with the Pyrex filter as with the slotted brass tube.

In our previous investigation at 25°C it was found that in the early stages the rate of disappearance of ethylene decreased as the pressure was increased. This was closely tied up with the rate of formation of acetylene and hydrogen as expressed in Eqs. (1)–(3). At higher temperatures, on the other hand, it was found that the rate of pressure decrease was greater at higher pressures. This is shown in Fig. 2.

That the effect of pressure on the rate of production of acetylene and hydrogen is not greatly different at high temperatures is shown in Figs. 3 and 4. Although the rate of production of both acetylene and hydrogen is greater at 300°C than at 25°C, it is seen that in both cases an increase in pressure results in a decrease in the rate of production of these products. At both
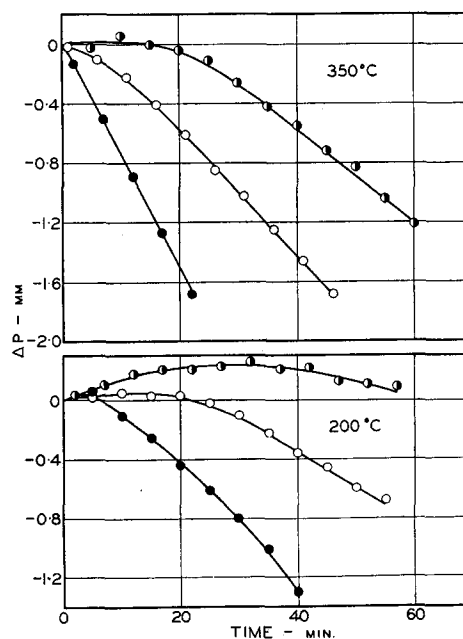

FIG. 2. Pressure change *vs.* time. ◑, 15 mm; ○, 30 mm; ●, 70 mm.

100-mm and 400-mm pressure the rate is greater at 300°C than at 25°C. The reason for this is clear when we realize that for a given pressure the number of deactivating collisions per second is less at 300°C than at 25°C. In other words, the rate of reaction (3) relative to that of (2) is greater at the higher temperature.

Figures 3 and 4 also show that at 300°C the rate of formation of hydrogen is greater than that of acetylene. This could be due to a number of causes. It must be remembered that in contrast to 25°C, the pressure is decreasing quite rapidly due to the formation of substances other than hydrogen and acetylene and there is always a possibility that hydrogen may be formed by secondary reactions. Another possibility is that acetylene may not be as inert at 300°C as it was at 25°C and that it may form a co-polymer with ethylene, for example.[13]

EFFECT OF NITRIC OXIDE ON THE REACTION

If, as seems to be the case, free radicals are formed in the initial stages of the reaction at high temperatures and reactions of these radicals are responsible for the rapid pressure decrease, then it is possible that polymerization might be inhibited by the presence of nitric oxide. Figure 5 shows the pressure changes in a series of runs at 15 mm-pressure and 300°C using various percentages of nitric oxide, namely, 0, 3 percent, 10 percent, and 19 percent. These curves have been shifted vertically by 0.5 mm to avoid congestion. In the presence of 10 percent or more of nitric oxide the initial rate of pressure *increase*
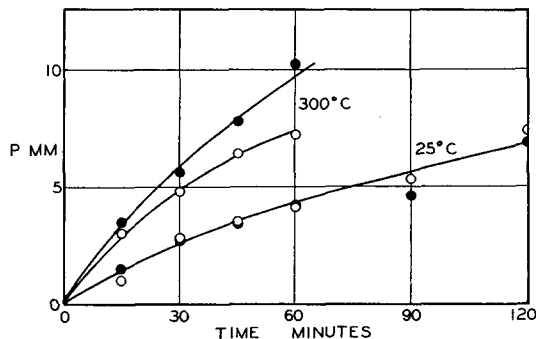
FIG. 3. Pressure of hydrogen and acetylene *vs.* time. ●, hydrogen; ○, acetylene. Initial pressure 100 mm.

[13] Naragon, Burk, and Lankelma, Ind. Eng. Chem. **34**, 355 (1942).

is practically identical with that at 25°C with no nitric oxide present (Fig. 6). That nitric oxide has little or no effect on the initial rate of pressure increase at 25°C is also shown in Fig. 6 where the pressure changes for a 14.7 percent mixture are given. It does, however, affect the height of the maximum, since at this pressure the maximum pressure increase is about 1.5 mm at 25°C.[6]

Products

A comparison of the products formed at 25°C and at 300°C is shown in Table I. The time is
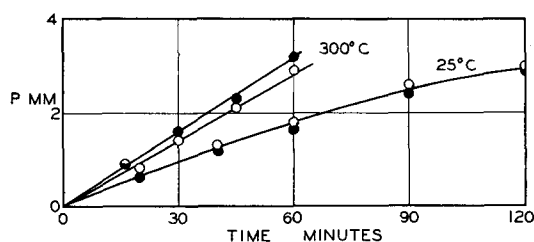
FIG. 4. Pressure of hydrogen and acetylene *vs.* time. ●, hydrogen; ○, acetylene; ◑, overlapping points. Initial pressure 400 mm.

given in minutes. The volume of higher products is in cc of liquid, that of the other products in cc of gas at 25°C and 760 mm. Hydrogen was removed and measured as previously described. Ethylene and acetylene were distilled off and acetylene determined in the mixture. In order to get enough products for a distillation, four runs were made at 25°C and the products (other than ethylene, acetylene, and hydrogen) combined.

The most interesting thing about these runs is that propylene is formed in relatively large amounts at 300°C, although none was found at room temperature. Furthermore, as might be expected, for the same yield of acetylene the production of "higher liquids" is greatly increased.

An idea of the amount of ethylene used up in processes other than the production of hydrogen and acetylene is obtained from the data in Table II. This table gives further information on the runs shown in Figs. 3 and 4. The initial pressure p and the pressure increase Δp are in mm. V_0 is the original volume of ethylene, V_{cond} is the volume of gas condensible in liquid air at the end of the run, and $V_{C_2H_2}$ is the volume of
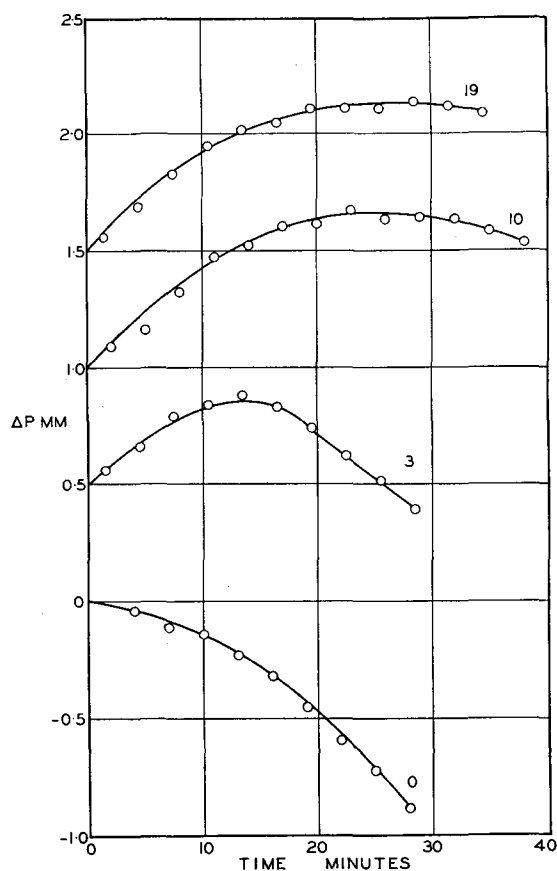
FIG. 5. Pressure change *vs.* time in the presence of nitric oxide. Initial pressure 15 mm, 300°C.

acetylene produced, all in cc at 25°C and 760 mm. If the average molecular weight of the products is high, the volume of ethylene used up by processes other than the production of hydrogen and acetylene is given by $V_0 - V_{cond}$. If the average molecular weight corresponded to C_4 it would be twice this. While the accuracy of such measurements is not high it is clear that the quantum yield of ethylene disappearance by these other processes is greater at 300°C than at 25°C by a factor of five to ten.

DISCUSSION

As we have mentioned above, there appears to be little doubt that the reactions leading to the formation of hydrogen and acetylene are not changed on raising the temperature. That is to say, their rate of production is determined by reactions (1), (2), and (3). Whether hydrogen is produced by reactions other than (3) or whether

acetylene is used up is not certain although it appears from Fig. 3 that the latter is more probable. In the reaction of $Cd(^1P_1)$ atoms with ethylene[7] it was found that acetylene formation dropped off as a run progressed till it reached a constant value. Further comparison shows that in both cases the ratio of pressure decrease to acetylene formation increased with increasing pressure, the actual ratios being of the same order of magnitude for $Hg(^3P_1)$ and $Cd(^1P_1)$ atoms under similar conditions of temperature.

In our discussion of the reaction of $Cd(^1P_1)$ atoms with ethylene[7] we were forced to the conclusion that reactions of the type (1)–(3) alone could not account for the results even in the early stages of the reaction. The complete absence of any initial pressure rise indicated that primary processes other than those corresponding to (1)–(3) must occur. If the pressure decrease were due solely to the onset of the hydrogen atom sensitized polymerization of ethylene, as found in the later stages of the $Hg(^3P_1)$ reaction at room temperature, and if the only process leading to the formation of hydrogen atoms were the reaction

$$M^* + H_2 \rightarrow 2H + M, \qquad (4)$$

then the initial pressure decrease could not be explained. Even a large increase in the quantum yield of the hydrogen atom sensitized polymerization of ethylene would not eliminate at least a small pressure increase until the concentration of molecular hydrogen was sufficient to permit it quenching the $Cd(^1P_1)$ or $Cd(^3P_1)$ atoms.

Similar considerations to those above apply to the $Hg(^3P_1)$ reaction at high temperatures. Just as we were forced to assume the reaction

$$Cd(^1P_1) + C_2H_4 \rightarrow C_2H_3 + CdH, \qquad (5)$$

so we believe that the high temperature results with $Hg(^3P_1)$ atoms can be accounted for on the

TABLE I. Initial pressure = 150 mm.

No.	Temp.	Time	C_2H_2	H_2	C_3H_6	C_4	Higher
179	300	180	22.3	33.6	50.5	13.5	0.21
180	300	229	24.2	38.2	49.0	18.0	0.26
172	25	247	28.0	39.0			
173	25	239	22.9	37.4	0	37.0	0.09
174	25	248	20.1	34.2			
175	25	243	19.7	32.2			

assumption that the reaction

$$Hg(^3P_1)+C_2H_4 \rightarrow C_2H_3+H+Hg(^1S_0) \quad (6)$$

or

$$Hg(^3P_1)+C_2H_4 \rightarrow C_2H_3+HgH \quad (7)$$
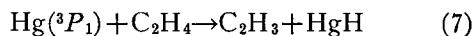
takes place. At 25°C the early stages of the reaction were accounted for quantitatively by reactions (1)–(3). However, we mentioned that at higher pressures there was evidence of polymerization occurring by some other process. This effect is further brought out in our present work. In Table II it can be seen that at 25°C there was some ethylene disappearing by reactions other than the formation of hydrogen and acetylene even when the concentration of molecular hydrogen was small.

Polymerization of ethylene sensitized by hydrogen atoms and vinyl radicals would be expected to be more rapid at high pressures.

It is quite possible, then, that reaction (6) or (7) did occur at 25°C, although to a much smaller extent than reactions (1), (2), and (3). The number of $Hg(^3P_1)$ atoms leading to reactions (6) or (7) must be relatively small since the quantum yield at 25°C and 13 mm was 0.37 and if we allow for loss of $Hg(^3P_1)$ atoms by reaction (1) followed by (2) it is clear that the number available for reactions (6) or (7) cannot be very large.

There are two possible ways of explaining the

increase in quantum yield and the absence of an initial pressure rise at high temperatures: (1) We can assume that the number of $Hg(^3P_1)$ atoms used up in reactions (6) or (7) is increased or (2) the quantum yield of the hydrogen atom and vinyl radical sensitized polymerization of ethylene is higher at high temperatures. The latter seems the more likely since the production of hydrogen and acetylene appears to be independent of temperature. In either case polymerization would be inhibited by nitric oxide.
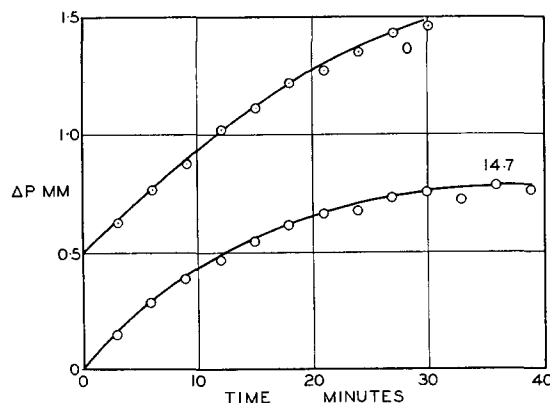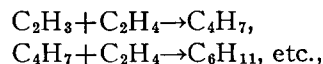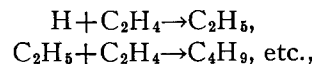

FIG. 6. Pressure change *vs.* time in the presence of nitric oxide. Initial pressure 15 mm, 25°C.

No direct evidence has ever been found for the existence of the vinyl radical, although Eltenton[14] was able to detect the allyl radical in the reaction of methyl radicals with propylene. He attributed his inability to detect the vinyl radical to its high reactivity. One would not expect to find any appreciable quantity of products with the empirical formula, C_nH_{2n-2} (other than acetylene). The large quantum yield of the sensitized polymerization of ethylene coupled with the fact that only one diene molecule would be found for each vinyl radical produced in reactions (6) or (7) would make it practically impossible to detect such compounds.

We can then assume that the large quantum yield at high temperatures is due to reactions of the type

$$C_2H_3+C_2H_4 \rightarrow C_4H_7,$$
$$C_4H_7+C_2H_4 \rightarrow C_6H_{11}, \text{ etc.,}$$

and

$$H+C_2H_4 \rightarrow C_2H_5,$$
$$C_2H_5+C_2H_4 \rightarrow C_4H_9, \text{ etc.,}$$

TABLE II.

No.	Temp.	p	Time	Δp	V_0	V_{cond}	$V_{C_2H_2}$	$V_0 - V_{cond}$
201	300	400	16	$-17._0$	185_0	178_3	4.1	6_7
202	300	400	30	$-28._3$	183_0	169_9	6.4	13_1
204	300	400	45	$-37._7$	186_5	168_0	9.8	18_5
203	300	400	60	$-50._0$	185_0	158_8	13.5	26_2
206	300	100	15	$- 7._0$	46_0	41_2	13.9	4_8
207	300	100	30	$-12._5$	46_0	37_4	22.0	8_6
209	300	100	45	$-19._5$	46_0	33_2	29.4	12_8
208	300	100	64	$-27._5$	46_0	28_9	33.0	17_1
216	25	400	20	$+ 0._5$	197_5	196_2	3.9	1_3
217	25	400	40	$- 1._5$	197_5	195_0	6.4	2_5
218	25	400	60	$- 1._0$	198_0	195_0	8.7	3_0
219	25	400	90	$- 1._0$	197_2	194_2	12.9	3_0
220	25	400	120	$- 2._0$	196_0	190_8	14.8	5_2
210	25	100	15	$0._0$	49_5	48_2	4.8	1_3
211	25	100	30	$+ 1._0$	49_4	48_2	13.8	1_2
213	25	100	45	$+ 1._0$	49_7	47_4	17.4	2_3
214	25	100	60	$+ 1._0$	49_4	46_7	20.2	2_7
215	25	100	90	$+ 1._0$	49_4	46_8	26.2	2_6
212	25	100	120	$0._0$	49_4	44_8	36.6	4_6

[14] G. C. Eltenton, J. Chem. Phys. **10**, 403 (1942).

TABLE III.

| Sensitizer	Wavelength	Excitation energy	Heat of formation of hydride	Quenching cross section	Remarks
Na(^2P)	5890 5896	48.3	51.6	44.0[a]	No reaction[b]
Cd($^3P_1$)	3261	87.3	15.5	26.5[c]	Slow reaction
Zn($^3P_1$)	3076	92.5	23.1	?	Slow reaction
Hg($^3P_1$)	2537	112.2	8.5	48.0[d]	Fast reaction
Cd($^1P_1$)	2288	124.4	15.5	High "absorption"	Fast reaction
Zn($^1P_1$)	2139	133.4	23.1	High "absorption"	Fast reaction

[a] R. G. W. Norrish and W. MacF. Smith, Proc. Roy. Soc. **A176**, 295 (1940).
[b] J. C. Jungers and H. S. Taylor, J. Chem. Phys. **4**, 94 (1936).
[c] E. W. R. Steacie and D. J. LeRoy, unpublished.
[d] E. W. R. Steacie, Can. J. Research **B18**, 44 (1940).

together with chain transfer and the usual chain stopping steps of radical recombination and decomposition. The formation of propylene at high temperatures is probably the result of the decomposition of butyl radicals by the reaction

$$C_4H_9 \rightarrow C_3H_6 + CH_3.$$
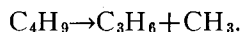
This would be more important at 300°C than at 25°C and would tend to increase the quantum yield due to the methyl radical sensitized polymerization of ethylene.

In this connection it is interesting to note that in the Zn($^1P_1$) photosensitized reactions of ethylene, propylene was one of the most important products. It was not formed in very large amounts in the Cd($^1P_1$) reactions, however, a fact which does not have any immediate explanation.

Apart from this one fact, the present investigation brings all the work on the photosensitized polymerizations of ethylene into line. These investigations are summarized in Table III. Where quenching data are known they are

given in A². A "slow" reaction indicates that the quantum yield is of the order 0.01 to 0.05. Energies are in kcal.

It will be seen that the reaction with Na(^2P), Cd($^3P_1$), and Zn($^3P_1$) atoms is very slow in spite of the large quenching cross sections, the energies apparently being too small. On the other hand, the reaction with Hg($^3P_1$), Cd($^1P_1$), and Zn($^1P_1$) atoms is quite rapid. Furthermore, the mechanism for these latter reactions now appears to be identical for the three cases, namely,

$$M^* + C_2H_4 \rightarrow C_2H_3 + H + M$$

or

$$\rightarrow C_2H_3 + MH,$$
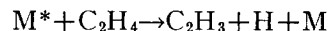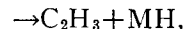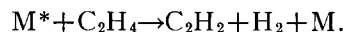
followed by an H atom and vinyl radical sensitized polymerization of ethylene.

In addition, acetylene is probably formed in all cases by the over-all process

$$M^* + C_2H_4 \rightarrow C_2H_2 + H_2 + M.$$

It should, of course, be emphasized that relating excitation energies to bond strengths is a drastic approximation. Any precise treatment of the transfer of energy from a sensitizer to a reactant must involve a detailed consideration of the transition states.[15] However, the fact that the reactions of Hg($^3P_1$) atoms fall in with those of the high energy group, in spite of the difference in multiplicity, indicates that the approximation of a simple transfer of energy is not inconsistent with the data on ethylene.

The authors would like to express their indebtedness to Mr. A. VanWinckel for assistance in carrying out the experiments.

---

[15] K. J. Laidler, J. Chem. Phys. **10**, 34, 43 (1942).