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Zinc Photosensitized Reactions of Ethylene

H. HABEEB, D. J. LEROY, AND E. W. R. STEACIE

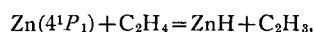
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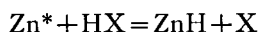
An investigation has been made of the polymerization of ethylene photosensitized by zinc, both resonance lines, 2139A and 3076A, being used. With $\lambda 3076$ the rate of the reaction is very small, and it is concluded that this is probably due to inefficient quenching. With $\lambda 2139$ a rapid polymerization occurs. The products of the reaction are propylene, butene, and small amounts of higher hydrocarbons. Acetylene formation is negligible. The rate of polymerization increases rapidly with increasing ethylene pressure. While there is some doubt about the mechanism, the most plausible suggestion seems to be that the initial step is



and that this is followed by an atom and free radical sensitized polymerization of ethylene.

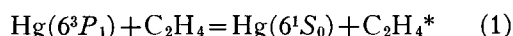
INTRODUCTION

IN a number of recent papers we have described investigations of cadmium photosensitized reactions.¹⁻⁴ The present paper is concerned with photosensitization by zinc, both resonance lines 2139A and 3076A being employed. The excitation energies of the states involved are 133.4 and 92.5 kcal. for Zn (4^1P_1) and Zn(4^3P_1), respectively, as compared with 124.4 and 87.3 kcal. for Cd(5^1P_1) and Cd(5^3P_1), and 112.2 for Hg(6^3P_1). In addition the heat of formation of ZnH is considerably higher than that of the other hydrides (23.1 kcal. for ZnH, 15.5 kcal. for CdH, and 8.5 kcal. for HgH). As a result processes of the type



will be possible provided that the strength of the H-X bond is lower than 156.5 kcal. for Zn(1^1P_1) and 115.6 kcal. for Zn (3^1P_1).

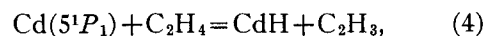
Much previous work has been done by other methods on the photochemistry of ethylene. In the case of the mercury photosensitized reaction, at least at low temperatures, it seems to be definitely established that the primary step is:⁵



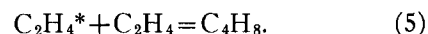
followed by



With cadmium (1^1P_1) atoms the evidence favors¹ a primary step which is at least in part



although the possibility of a reaction analogous to (1) is not excluded. The reaction photosensitized by Cd(5^3P_1) atoms has a relatively low quantum yield, and hence not much definite information exists, but it appears probable that what reaction does occur involves a direct polymerization, by a mechanism such as (1) and (2) together with



This is not unexpected since the excitation energy of Cd(5^3P_1) atoms is probably too small to permit reactions analogous to either (3) or (4) to occur. (See (3) for a discussion of this point.)

EXPERIMENTAL

The Light Source

The zinc resonance lamp was of the high voltage, low pressure type, with neon as a carrier. It was similar in all essential details to

¹ E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.* **10**, 22 (1942).

² E. W. R. Steacie, D. J. LeRoy, and R. Potvin, *J. Chem. Phys.* **9**, 306 (1941).

³ E. W. R. Steacie, *Ann. N. Y. Acad. Sci.* **41**, 187 (1941).

⁴ E. W. R. Steacie and R. Potvin, *Can. J. Research* **B18**, 47 (1940); *J. Chem. Phys.* **7**, 782 (1939).

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

the cadmium lamps which we have previously described,¹ except that it was necessary to operate at a somewhat higher temperature on account of the lower vapor pressure of zinc.

A set of spectrograms of the lamp is shown in Fig. 1. These were taken with an Eastman 40 U.V. sensitized plate. Actually $\lambda 2139$ is more intense than $\lambda 3076$, but this is masked by the falling off in plate sensitivity in the short ultraviolet. It is evident that the lamps are a highly efficient source of the two zinc resonance lines. The cadmium resonance lines, 3261A and 2288A, and the mercury line at 2537A appear also, but are much too weak to have any appreciable effect.

The behavior of the lamps was by no means as satisfactory as that of cadmium lamps. We have had several of the latter with lives of over 1000 hours. With zinc the average life was quite short, less than 50 hours. Failure occurred either at the lead-in wires or at the graded seal, usually the former. It appears probable from an examination of broken lamps that the zinc vapor destroys the "coating" on the electrodes. This decreases their effective surface, and the electrodes run continually hotter until failure occurs by cracking at the lead-in wire. This suggests that the life might be much longer at lower currents, and in the last lamp used a current of 40 ma was used instead of 120 as formerly. This appeared to give much more satisfactory operation. It appears likely that where high intensities are not so essential very much longer life could be obtained by operating at 15 ma.

As a result of difficulties with the lamps it was not possible to obtain as reproducible results as would have been desired, although the output of any given lamp was satisfactorily constant up to very shortly before its failure. Also the short life of the lamps made it impracticable to carry out a succession of long runs for the purpose of accumulating products. This was especially true in the case of runs with $\lambda 3076$ since the reaction in this case was very slow.

In experiments with the long-wave resonance line at 3076A a filter consisting of an 18-inch length of Corex D tubing with a wall thickness of approximately 2.3 mm was slipped over the entire lamp. This completely removed the lower resonance line. Since, as will appear subsequently, the effect of $\lambda 3076$ was slight compared

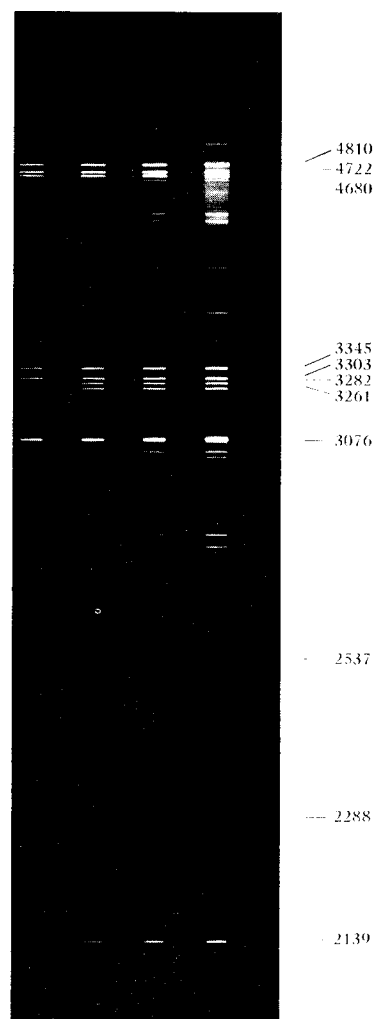


FIG. 1. Spectrogram of zinc lamp. Successive exposures 4, 12, 60, 300 sec.

with that of $\lambda 2139$, the experiments with $\lambda 2139$ were done with the full radiation from the lamp. The output of the lamp was determined only by a very rough geometrical estimate, and indications were that the amount of $\lambda 2139$ entering the reaction system was of the order of 10^{-7} Einstein per sec.

Information on the quenching of zinc resonance radiation is entirely lacking. Failing this, some rough "absorption" measurements were made. Owing to difficulties associated with imprisonment of radiation and pressure broadening such measurements are difficult to interpret. They do, however, give a qualitative indication of the fraction of the incident energy which is

absorbed by the sensitizer and transferred to the reactant. The results obtained indicated a very strong absorption of $\lambda 2139$ in the presence of ethylene, over 95 percent of the incident radiation being absorbed in the presence of 100 mm of ethylene, with a zinc vapor pressure corresponding to 310°C, and a light path of approximately 4 cm. The absorption of $\lambda 3076$ by ethylene was comparatively slight, not over 4.5 percent being absorbed in the presence of 200 mm of ethylene. There thus appears to be a very strong decrease in the quenching efficiency of ethylene for 3P_1 atoms as we go down the series Hg, Cd, Zn, in spite of the increasing lifetime of the excited state. Absorption of $\lambda 3076$ in the presence of hydrogen was also surprisingly small, and was not very much greater than that of ethylene under comparable conditions. This is unexpected in view of the fact that Bender⁶ obtained resonance excitation of the ZnH bands when a mixture of zinc vapor and hydrogen was illuminated with the radiation from a zinc-hydrogen lamp containing $\lambda 3076$. $\lambda 2139$, however, did not give rise to ZnH bands under these conditions. Further discussion of this point will be deferred since it is planned to investigate the quenching in the near future.

The Reaction System

The reaction system was the same as that previously employed.¹ The lamp was contained in a cylindrical furnace which was heated electrically. It was surrounded by an annular fused quartz reaction vessel, 10-cm length, 8-cm diameter, with a 4-cm diameter hole through the middle. The reaction vessel was connected to a saturator containing zinc turnings, which was contained in a separate furnace. (In some preliminary runs a 1 : 1 zinc-tin alloy was used in the saturator. This is liquid at the temperatures employed. However, the turnings proved to be more efficient and convenient.)

For circulating runs a pump passed the gas through the saturator and then through the reaction vessel and traps to condense out higher boiling products. For static runs the tubing between the saturator and the reaction vessel was sealed off, and zinc turnings were placed directly in the reaction vessel. The total apparent

volume of the circulating system at 310°C was about 2 liters, and that of the static system was 558 cc. In the circulating runs the rate of circulation was about 500 cc per minute.

Analysis

The gaseous products of the reaction were analysed by distillation in a small-capacity Podbielniak type still. Acetylene was determined as previously described.⁵

Materials

The zinc used was British Chemical Standard grade, and contained 99.95 percent zinc, and about 0.01 percent cadmium.

Ethylene was obtained in cylinders from the Ohio Chemical and Manufacturing Company. It was purified by bulb to bulb distillation, and the resulting gas contained no impurities detectable with the analytical methods used.

Hydrogen was taken from commercial cylinders and was purified by passage over platinized asbestos at 600°C, and through a liquid-air trap.

RESULTS

Most of the work reported here was done with the lower resonance line, 2139A. On account of the small quenching of the 3076A line it was not possible to make a very thorough investigation with it, and the results obtained may be regarded as only semiquantitative.

(A) Photosensitization by 1P_1 Atoms ($\lambda 2139$)

The results of a typical series of static runs at 310°C without the Corex D filter are given in Fig. 2. As will be shown later, the effect produced by $\lambda 3076$ is negligible compared with that due to $\lambda 2139$, and hence the results given in Fig. 2 are, within the experimental error, due to $\lambda 2139$ only. It will be seen that there are no indications of an initial pressure rise, as occurs with the mercury photosensitized reaction, and that the pressure decrease in the early stages of the reaction is a linear function of the time.

As shown by Fig. 2, and better by Fig. 3, the initial rate of pressure decrease increases rapidly with increasing pressure. In view of the efficient absorption of $\lambda 2139$ in the presence of ethylene this effect cannot be ascribed to increased quenching at the higher pressures, and must be

⁶ P. Bender, Phys. Rev. **36**, 1543 (1930).

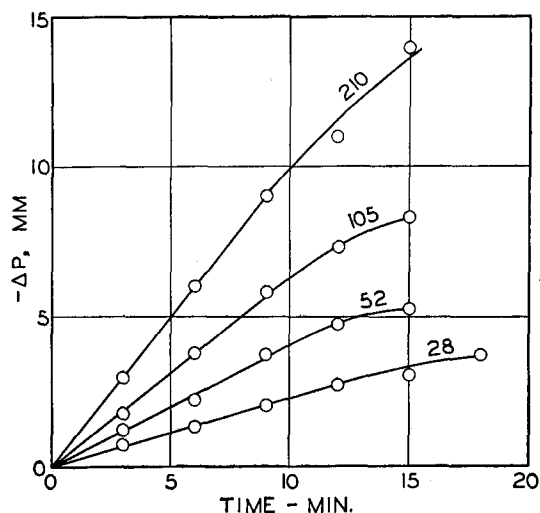


FIG. 2. Experiments with $\lambda 2139$. Static system at 310°C . Ethylene pressures in mm, as indicated on the curves.

due to an increase in the rate of the polymerization itself.

Blank runs indicated no appreciable thermal reaction under the conditions used, and possible catalytic effects due to zinc or traces of zinc oxide are thus ruled out.

The Products of the Reaction Acetylene

In view of the importance of acetylene as a product in the mercury photosensitized reaction, analyses for it were carried out in a number of cases by the method previously used.⁵ The results indicated that acetylene formation is of even less importance here than in the case of the cadmium photosensitized reaction. Even in static runs which were carried to a pressure drop of 50 percent, analyses showed amounts of acetylene of the order of 0.1 percent or less. Acetylene formation is thus negligible compared with polymerization.

Hydrogen

A very small amount of non-condensable gas was observed. This was very roughly equal in amount to the acetylene formed, and it was assumed to be hydrogen.

Condensable Products

A number of circulating runs at 310°C were made for the purpose of collecting condensable

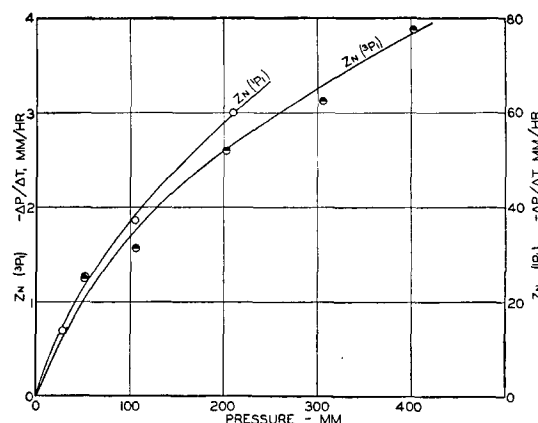


FIG. 3. Initial rates of reaction. Static system. Temperature 310°C for runs with $\lambda 2139$, 320°C for runs with $\lambda 3076$.

products for analysis. The gases in the reaction system were circulated during these runs through a trap which was maintained at -125° to -130°C . In these experiments the initial ethylene pressure was approximately 200 mm, but the pressure during the run with the trap cold was less than this owing to the condensation of ethylene in the trap, and the actual pressure was thus the vapor pressure of ethylene at the trap temperature, *viz.*, about 120 mm.

In a typical run the pressure decrease, after warming the trap to room temperature, was 78 mm in 7.2 hours. The products were analyzed by low temperature fractional distillation with the result shown below:

	cc at N.T.P.
$\text{H}_2 + \text{CH}_4$	trace
C_3H_6	87
C_4H_8	31
Higher	~30

The distillation curve for this run is shown in Fig. 4. The production of propylene as a major product was established beyond doubt. The distillation curve was absolutely flat over a range of 72 cc, and this fraction was again distilled separately with the same result. It was then analyzed by combustion by the method of Marion and Ledingham.⁷ The carbon-hydrogen ratio agreed with that of an olefin to within less than 1 percent. The molecular weight was found to be 39.2 as compared with 42 for propylene and 28 for ethylene. There seems to be no doubt, therefore, that the gas is mainly propylene.

⁷ L. Marion and A. E. Ledingham, *Ind. Eng. Chem. Anal. Ed.* **13**, 260 (1941).

A number of other circulating runs gave results in agreement with the above, in every case propylene being a major product, together with butenes and small amounts of higher hydrocarbons.

Several blank runs were made in which ethylene was circulated in the apparatus with the lamp off for periods up to 24 hours. In all of these there was a negligible pressure change and no indication of either propylene or non-condensable gas.

(B) Photosensitization by 3P_1 Atoms ($\lambda 3076$)

The results of a series of static runs at 320°C with $\lambda 3076$ are shown in Fig. 5, and the initial rates, together with those for $\lambda 2139$, are given in Fig. 3. The rates for the two resonance lines in Fig. 3 are not directly comparable since the two series of experiments were made with different lamps.

A series of runs at 200-mm pressure with the same lamp indicated that the relative rates of pressure decrease for $\lambda 2139$ and $\lambda 3076$, allowing for the decrease in intensity of $\lambda 3076$ due to the transmission of the filter, were in the ratio of 8/1. An estimate of the relative intensities of the two lines was made using a sodium photo-tube of known wave-length sensitivity and various combinations of chlorine and Corex D filters of known transmission. This indicated that $\lambda 2139$ was approximately twice as intense as $\lambda 3076$. These measurements are somewhat uncertain since corrections must be made for other lines near those in question. However, photographic

estimates indicated that the total intensity of 3261A, 3282A, 3303A, and 3345A was less than 10 percent that of 3076A, and that all other lines in the short ultraviolet were less than 0.5 percent of the intensity of $\lambda 2139$. The ratio of the rates with $\lambda 2139$ and $\lambda 3076$ for equal intensities is thus approximately 4/1, or for equal numbers of quanta approximately 6/1. In view of the small absorption of $\lambda 3076$ by ethylene, and the very high absorption of $\lambda 2139$, the entire difference in rates could be accounted for on the basis of poor quenching of $\lambda 3076$ by ethylene. In any case, it is apparent that the quantum yield for the Zn(3P_1) sensitized reaction is much higher than that for the Cd(3P_1) reaction.

(C) Ethylene-Hydrogen Mixtures

A number of static runs were made with ethylene-hydrogen mixtures at 320°C. With $\lambda 3076$ the relative rates of pressure decrease with 20 cm C₂H₄ alone and with 20 cm of C₂H₄+20 cm of H₂ were in the ratio of 1 : 21. There is thus a much faster reaction in the presence of hydrogen, and at least part of the increase can be attributed to more efficient quenching by hydrogen. However, it seems certain that the whole effect cannot be explained in this way, and that the quantum yield for the reaction with ethylene-hydrogen mixtures must be considerably higher than that for ethylene alone. In view of Bender's work, the mechanism for the reaction in the presence of hydrogen is obviously

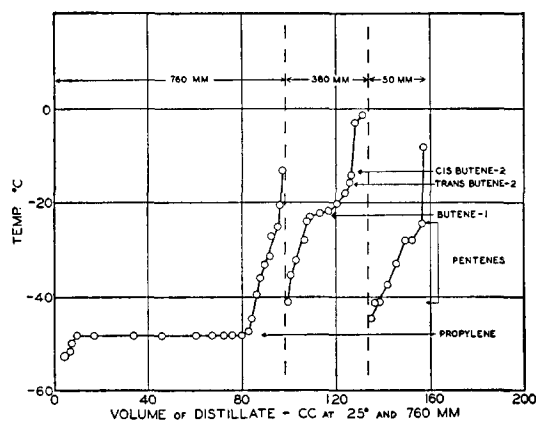
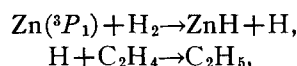


FIG. 4. Distillation curve of products from circulating run with $\lambda 2139$.

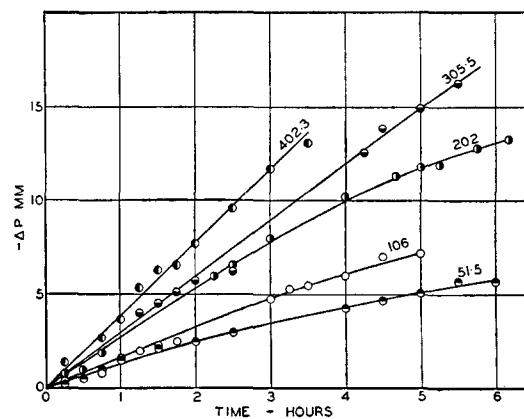


FIG. 5. Experiments with $\lambda 3076$. Static system at 320°C. Ethylene pressures in mm, as indicated on the curves.

followed by a free radical sensitized polymerization of ethylene.

No acetylene could be detected in the products of these runs. A distillation analysis of the products of a typical circulating run is given below:

Temperature	320°C	
Time	10½ hours.	
Initial pressures (trap at room temp.)	H ₂ = 126.5 mm C ₂ H ₄ = 126.0 mm Total = 252.5 mm.	
Final pressure (trap at room temp.)	= 215 mm.	
	Products, cc at N.T.P.	
	Initial	Final
H ₂	407	376
C ₂ H ₄	405	169
C ₃ H ₆	—	54
"C ₄ "	—	14
Higher	—	14
CH ₄	—	≤4

The products are thus very similar to those found with λ2139 and ethylene alone.

A few runs were also made with ethylene-hydrogen mixtures using the full radiation from the lamp. From Bender's work it appears that the quenching of the 2139A line by hydrogen is very small. Since the indications from our absorption measurements are that 3076A is only slightly quenched by ethylene while 2139A is very strongly quenched, it follows that in an ethylene-hydrogen mixture illuminated with both resonance lines the hydrogen should quench λ3076 and the ethylene λ2139. Hence the rate would be expected to be approximately the sum of the rates for an ethylene-hydrogen mixture illuminated with λ3076 and for ethylene alone illuminated with the full radiation of the lamp.

The relative rates obtained in a typical series of runs are given below in arbitrary units.

Line	Reactant	Relative Rate
3076	C ₂ H ₄	0.048
3076+2139	C ₂ H ₄	0.28
3076	C ₂ H ₄ +H ₂	1.00
3076+2139	C ₂ H ₄ +H ₂	1.20

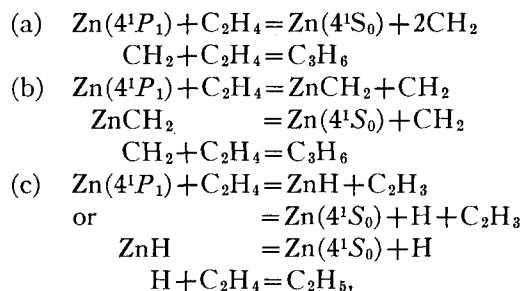
It will be seen that the sum of the rates in lines 2 and 3 is 1.28, as compared with 1.20 for line 4.

DISCUSSION

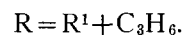
(A) Zn(4¹P₁) + C₂H₄

In a general way the reaction resembles that with Cd(5¹P₁) atoms. The main difference in the

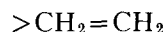
results with zinc is the fact that propylene is a major product of the reaction. Since, in the circulating system, the trap would quite efficiently remove butenes and all products of higher molecular weight, it appears that propylene cannot arise by secondary reactions of the stable products. It can, of course, arise by secondary reactions of short-lived substances. The main possibilities for the mechanism of its formation appear to be the following:



followed by the building up of larger alkyl radicals by successive additions of ethylene, and their ultimate breakdown by



The main difficulty with (a) is the energy requirement. The excitation energy of Zn(4¹P₁) is 133.4 kcal. While there is considerable doubt about the strength of the C=C bond in ethylene, it appears unlikely that it is less than 145 kcal. and it may be somewhat higher than this. There is, however, the possibility that one or both of the methylenes should be formed as a molecule and not a radical, as has been suggested in other cases.⁸ It appears probable that the change



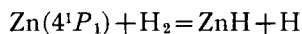
is exothermic to the extent of about 37 kcal.,⁹ and the over-all process (a) would thus become energetically possible.

As far as (b) is concerned, there appears to be no information about the existence of compounds such as ZnCH₂. If such a compound exists with a heat of formation of 10–20 kcal. then (b) would be energetically possible. Such a process

⁸ R. G. W. Norrish, H. G. Crone, and O. D. Saltmarsh, *J. Chem. Soc.* **1933**, 1533; J. E. Lennard-Jones, *Trans. Faraday Soc.* **30**, 70 (1934); R. G. W. Norrish, *ibid.* **35**, 191 (1939).

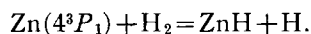
⁹ W. Heitler and G. Herzberg, *Zeits. f. Physik* **53**, 52 (1929).

might occur with a high efficiency since the energy balance would be relatively exact. (The non-occurrence of the corresponding process⁶



is probably to be ascribed to the large energy discrepancy, approximately 45 kcal. being available in excess of the energy required.)

It seems probable that the real explanation is (c). The most significant evidence in this connection is the comparison of the products of the reaction of ethylene photosensitized by $\lambda 2139$ with those of ethylene-hydrogen mixtures photosensitized by $\lambda 3076$. It will be seen that the products are very similar, and that propylene is a major product in the latter case as well. Now there is no question that there is insufficient energy to break the C=C bond in the case of $\lambda 3076$. Further, in the case of $\lambda 3076$ the reaction is very much faster with C₂H₄-H₂ mixtures than it is with ethylene alone. Hence it must be assumed that the primary step is almost exclusively



Propylene must therefore ultimately arise from reactions initiated by hydrogen atoms. It therefore seems reasonable to assume that it arises in a similar manner in the case of $\lambda 2139$ with ethylene alone, i.e., by mechanism (c).

The only difficulty with this mechanism is the fact that propylene is not formed in appreciable amounts in the reaction photosensitized by Cd(5^1P_1) atoms,¹ where the evidence points to a primary step analogous to (c). However, it has been pointed out that the results on the cadmium photosensitized reaction are also explainable in terms of a primary step involving the formation of an excited molecule.

The fact that the rate of polymerization increases with increasing ethylene pressure is in line with other investigations in which polymerization of ethylene proceeds by a free radical mechanism. Examples of this behavior are the cadmium photosensitized reaction,¹ the acetone photosensitized reaction,^{10,11} the reaction photo-

sensitized by aldehydes,¹¹ and the reaction induced by the thermal decomposition of azomethane.¹² It is significant that in the case of the mercury photosensitized reaction at room temperature, where free radicals are not involved, at least in the early stages,⁵ the initial rate of the reaction *decreases* with increasing ethylene pressure.

(B) $\text{Zn}(4^3P_1) + \text{C}_2\text{H}_4$

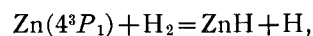
In view of the semiquantitative nature of the results, and the absence of information about the products, speculation about the mechanism of the reaction is hardly justified. It may, however, be pointed out that there is ample energy available for the reaction



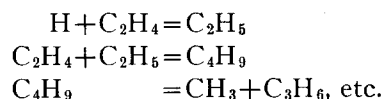
The low reaction rate is apparently due to inefficient quenching of $\lambda 3076$ by ethylene, and further discussion will be deferred until information on quenching is available.

(C) $\text{Zn}(4^3P_1) + \text{C}_2\text{H}_4 + \text{H}_2$

As pointed out above, there is little doubt that the primary process in this case is



and that this is followed by a hydrogen atom sensitized polymerization of ethylene, i.e.,



The authors wish to express their indebtedness to Professor C. A. Winkler for his advice and assistance, to Mr. A. Van Winkel for assistance in carrying out the experiments, and to Mr. A. E. Ledingham for making the micro-analyses. One of them (H.H.) is indebted to the National Research Council of Canada for a Studentship, during the tenure of which part of this work was performed.

¹⁰ H. S. Taylor and J. C. Jungers, Trans. Faraday Soc. **33**, 1353 (1937).

¹¹ C. J. Danby and C. N. Hinshelwood, Proc. Roy. Soc. **A179**, 169 (1941).

¹² O. K. Rice and D. V. Sickman, J. Am. Chem. Soc. **57**, 1384 (1935).