ZINC PHOTOSENSITIZED REACTIONS
OF ETHYLENE.

by

Herbert Habeeb, BSc.

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GENERAL INTRODUCTION

To the alchemist it became an apparent fact that certain transmutations would proceed readily whereas others would not.

To the modern scientist the processes of transmutation of substances into other substances in the supra-atomic field — to be distinct from sub-atomic transmutations — would be a closed book; if by prededuced constants of the elements and compounds involved he could calculate the state of equilibrium for the transmutation, and by set general principles and rules he could determine the rate of transmutation.

The problem of determining the state of equilibrium of a reaction or transmutation belongs to the field of thermodynamics. This problem is today well on its way to being solved.

Though the state of equilibrium may permit a reaction to go, this does not say that it will

do so; for the rate of the reaction might be such as
to prevent the reaction from proceeding to a state
of equilibrium within a practical length of time.
The rules and general principals concerning reaction
rates are discussed under the heading of chemical-
kinetics.

A chemical reaction is in general the
resultant of a number of steps, and accordingly
the over-all rate of the reaction is no faster than
its slowest elementary step, i.e. THE RATE IS OFTEN
DEPENDENT ON INTERMEDIATE STEPS. These steps often
involve atoms and radicals. Accordingly much of the
work being done in chemical-kinetics today consists
of investigations of the reactions of atoms and
radicals.

The determination of what is the rate
governing process and especially the atoms and
radicals involved, and also correlated facts such
as life-times, probabilities of formation, and
energies of formation of these atoms and radicals,
has to be done by inference from analytical data
and data provided by instruments such as the
manometer, the spectrograph and the mass-spectro-
graph.

The Paneth mirror technique (1) has
definitively proved the existence of free-radicals,
so the study of the reactions of radicals and
atoms may be confidently carried on. The methods
used, that produce atoms or radicals, or show
evidence that they are produced, are:

The method of Wood and Bonhoeffer (2),

Photochemical action,

Photosensitization.

The subject matter to be discussed herein
belongs to that part of chemical-kinetics associated
with light and called photosensitization, and deals
with particle identification, i.e. trying to
isolate the elementary and rate determining step
of a reaction and the energy of activation necessary
for the step. To be more explicit, the subject
matter to be dealt with is the metallo-photosensi-
tization of the hydrocarbons, of which ethylene in
particular is to be intensively scrutinised.

PHOTOSENSITIZATION

ON the basis of thermodynamical reasoning,
in 1921, Klein and Rosseland(3) inferred that, if
ionizing and exciting collisions take place in an
assemblage of atoms and electrons, i.e. collisions
of the first kind, inverse processes must also take
place, namely, collisions between excited atoms
and electrons in which the excitation energy is
transferred to the electrons in the form of kinetic
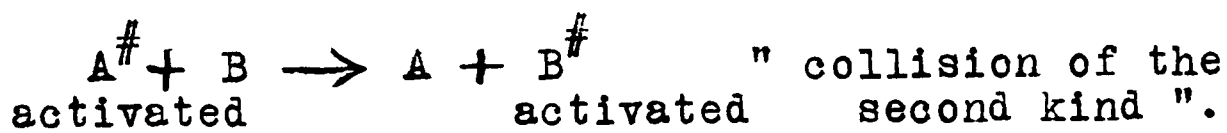energy. They called such collisions,"collisions of
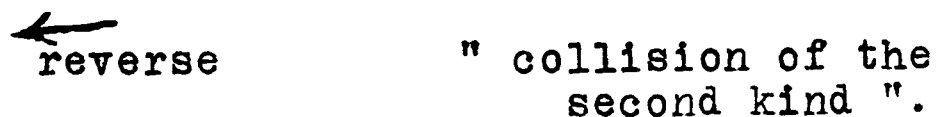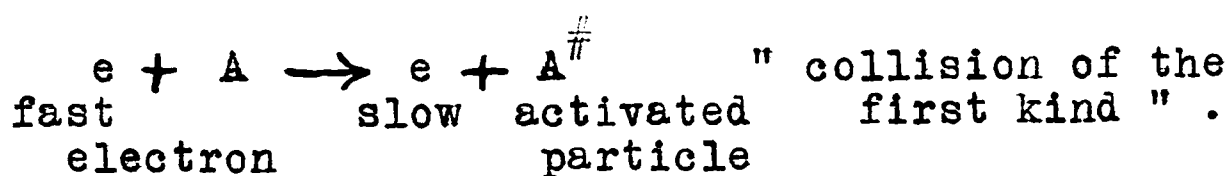the second kind".

An extension of this idea to include
collisions between two atoms or molecules was made
by Franck(4). He supposed that an excited atom
might collide with a normal atom or molecule and
give up a quantized whole or part of the energy
of excitation to the unexcited atom; the latter
might then take up the energy as translational
energy, excitational energy or both, there being

no loss of energy by radiation during the process.

This "collision of the second kind" is the fundamental physical principle underlying photosensitized chemical reactions. The exact mechanism of transference of energy in a "collision of the second kind" is open to doubt, but in spite of this it is possible to make considerable progress in dealing with photosensitized reactions.

As only the light which is absorbed can cause a chemical reaction to occur, it is obvious that beyond a certain maximum wave-lenth where absorption is nil, no photolysis will take place. This maximum wave-length, the photochemical threshhold, coincides in many cases with the beginning of a continuum or predissociation region (corresponding to an adiabatic transition from an attractive state to a repulsive or weakly attractive state (5)). So, to produce a reaction in a substance incapable of absorbing the light used, it is necessary to introduce into the system a substance capable of absorbing that light and which then will convey the energy to the reactants by a" collision of the second kind".

If this energy is sufficient to cause reaction and
if the light absorbing substance or sensitizer is
not transformed in any way, the process is known
as PHOTOSENSITIZATION .

$$e + A \longrightarrow e + A^{\#} \quad \text{" collision of the first kind " .}$$

fast   slow   activated
electron   particle

$$\longleftarrow \text{reverse} \quad \text{" collision of the second kind ".}$$

$$A^{\#} + B \longrightarrow A + B^{\#} \quad \text{" collision of the second kind ".}$$

activated   activated

A historical example of photosensitization
is that of the photosynthesis of carbohydrates by
chlorophyll in plants; dyes have long been used to
extend and modify the sensitive range of photographic
plates; and even pathological abnormalities or
diseases have been described, that are due to the
eating of a sensitizer by animals.

We may distinguish between two types of
photosensitization:

Type one has for the sensitizer a
substance which has an absorbing continuum which
covers the desired line or lines in the spectrum
of the light source utilized. E.g., if mixtures
of chlorine and ozone are illuminated by violet
light, light is absorbed by the chlorine, and the
ozone is decomposed with no net change in the
chlorine (6).

Type two has for the sensitizer the same
substance as that which is doing the emitting in
the light source, and since the sensitizer is/ in the
ground or normal state we will get an absorption
of only those lines whose energy of transition orig-
inated from the ground level, i.e. the resonance
lines.

As a matter of fact the number of atoms or
molecules in the first energy state above the ground
state (or any energy state) can be compared with
the number in the ground state itself (or any
other state) by means of the equation

$$\frac{n}{N} = \frac{p_n}{p_N} \cdot e^{-(E_n - E_N)/RT} \qquad .$$

Where n and N are the number of particles in the
first and normal states respectively;

p_n and p_N are the respective statistical weights of the states; and $E_n - E_N$ is the difference in energy between the states.

Now $\dfrac{p_n}{p_N} = 3$ for all resonance lines considered in this work excepting sodium where it is 1 or 2.

And for the cases considered

$$e^{-(E_n - E_N)/RT} \doteqdot e^{-100} \quad ,$$

i.e. $\dfrac{n}{N} = 3e^{-100}$ which is a very small and negligible number. Consequently the amount of energy absorbed by atoms in the first state would be negligible.

With the type two sensitizer we have a rather definite input of energy, since only a definite line is absorbed whereas type one will employ a certain band or range of wave-lengths.

Practical examples of type two are the metals mercury and cadmium and zinc. They possess suitable vapor pressures at employable temperatures, and the various energies in their resonance lines are sufficient to cause chemical reactions and decompositions.

The differences in energy content of these states is such that they can be used as points of reference in a determination of the energy of activation necessary for a reaction, see table I.

The process by which light energy is absorbed by the sensitizer, in this case the zinc atom, can be conveniently symbolised for the zinc $3076\overset{\circ}{A}$ resonance line thus:

$$Zn(4\,{}^{1}S_0) + h\nu(3076\overset{\circ}{A}) \longrightarrow Zn(4\,{}^{3}P_1) \, .$$
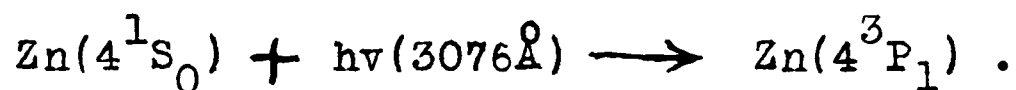
Milne[7] has shown that the rate of formation of excited atoms exposed to isotropic monochromatic radiation is a function of the lifetime of the excited atom and of the absorption of the vapor for the radiation in question.

TABLE I

EXCITATION ENERGIES, ETC.

Substance	Resonance Line, $\overset{\circ}{A}$	Transition	Energy of excited atom, kcal.	Heat of dissociation of hydride, kcal.	"Maximum energy available" to split off H atom, assuming intermediate hydride formation, kcal.
Mercury	1489	$6^1S_0 - 6^1P_1$	153.9	8.6	162.5
	2537	$6^1S_0 - 6^3P_1$	112.2	8.6	120.8
Cadmium	2288	$5^1S_0 - 5^1P_1$	124.4	15.6	140.0
	3261	$5^1S_0 - 5^3P_1$	87.3	15.6	102.9
Zinc	2139	$4^1S_0 - 4^1P_1$	133.4	19.6	153.0
	3076	$4^1S_0 - 4^3P_1$	92.5	19.6	112.1

The efficiency of the above symbolised process will depend largely, therefore, on the distribution of intensities of the exciting and absorption lines.

The emitted or exciting line from the resonance lamp will more or less possess all of the following broadenings:

1, Natural broadening due to the finite life-time of the excited state.

2, Doppler effect broadening due to the motions of the atoms.

3, Lorentz or pressure broadening due to collisions with foreign gases.

4, Holtsmark broadening due to collisions with similar atoms.

5, Stark effect broadening due to collisions with electrons and ions.

Whereas the absorption line will not possess the Stark effect broadening, but due to the/greater foreign gas pressure this lack will be made up for by a greater Lorentz or pressure broadening.

Thus it may be said that the distribution of intensities of the exciting and absorption lines are practically the same; and that the above process will be quite efficient for the purposes of this work.

Looking at table I we see that mercury has two resonance lines[#] 1849$\overset{o}{A}$ and 2537$\overset{o}{A}$ of 153.9 and 112.2 kcal. excitation energy respectively; ordinarily, the 1894$\overset{o}{A}$ is almost completely filtered out by the lamp wallsof quartz. And so for practical purposes we have only the 2537$\overset{o}{A}$ line of the mercury spectrum available for photosensitization.

Cadmium and zinc give lines such that both resonance lines are transparent to quartz; and in either case the lower resonance line ,i.e. the line in the farther ultra-violet, can be filtered out by using corex-D filters, as is shown by spectogram III. Cadmium's, lines, 2288$\overset{o}{A}$ and 3261$\overset{o}{A}$ have energies of 124.4 and 87.3 kcal.; while zinc's, lines,2139$\overset{o}{A}$ and 3076$\overset{o}{A}$ have 133.4 and 92.5 kcal. respectively.

[#]NOTE. Other resonance lines of lesser importance are in the extreme ultra-violet and are filtered out.

If the photosensitization is complicated by the formation of a metallic hydride; then the maximum energy available is the sum of the energy in the resonance state considered and the heat of formation of the respective hydride formed.

The present accepted values for the heats of formation of the respective hydrides are:

HgH	8.6	kcal.	reference	(8).
CdH	15.6	"	"	(9).
ZnH	19.6	"	"	(10).

In spectroscopic and discussions of this sort it is convenient to make a Grotrian diagram connecting the energies of various states with the quantum number of these states.

Mercury, cadmium and zinc belong to the same group in the periodic table and emit similar spectrum. The explanation is that each has two electrons in the outer electron-shell. The Grotrian diagram of each metal, therefore, will be the same except for the magnitude of energies in the corresponding states.

Since zinc has two electrons in its outer shell; it will, therefore, possess singlet and triplet systems. The combination principle along with the selection rules of quantum mechanics will give a number of permissable transitions, the most important of which are shown in figure I.#

The two lines connecting the zinc ground state 1S (or 4^1S_0) to the 2P (or 4^1P_1) and $2p_2$ (or 4^3P_1) states respectively correspond to the two resonance lines of zinc. And in this work both the 4^1S_0- 4^1P_1 and 4^1S_0- 4^3P_1 lines will be considered.

The transitions between both the $2p_1$ (or 4^3P_2) and $2p_3$ (or 4^3P_0) metastable states and the ground state 1S (or 4^1S_0) are forbidden.

The atom therefore, once in a metastable state, will stay in this state until it can give up its energy to a colliding body or acquire enough energy to jump to an upper level.

#NOTE. Figure I gives the original Grotrian diagram in which the quantum terms are out of date. Here the accepted terms are in bracketts, but otherwise will be used solely.

It is interesting to note that the energy difference between the 4^3P_0 metastable state and the 4^3P_1 state in zinc is very small, 0.024 volts; and is small compared to the energy required for the same transition in cadmium, 0.07 volts, and mercury, 0.21 volts. Consequently a zinc atom in the 4^3P_0 state can be readily raised to the 4^3P_1 state by a thermal collision, since the relative kinetic energy of the gas molecules or atoms present is 0.08 volts at $350^\circ C$.

Figure I ,

Grotrian diagram of zinc .

QUENCHING

The efficiency of a photosensitization depends on the efficiency of the energy transfer from the activated sensitizer to the reactant or one of the reactants, i.e. upon how many collisions, between sensitizer and reactant, are necessary before a successful transference of energy takes place.

In the study of resonance radiation, Wood(11) was first to note that mercury resonance radiation emitted from a cell containing Hg vapor and subjected to mercury arc radiation was reduced in intensity by the addition of a foreign gas. This process of reduction has been given the name of QUENCHING .

It is quite evident that the greater the quenching the more efficient is the photosensitization provided that the energy transferred in the process of quenching is sufficient to activate the reaction.

The amount of quenching in a given system will depend upon the life-time and nature of the excited atom, the concentration of the foreign molecules or reactants present, and the nature of the foreign molecules.

Table   II .

Atom	Series notation of resonance line.	Wave length in $\overset{o}{A}.$	Life-time in secs.
Hg	$6\,^1S_0 - 6\,^3P_1$	2537	$1 \cdot 10^{-7}$
	$6\,^1S_0 - 6\,^1P_1$	1489	$1 \cdot 10^{-9}$
Cd	$5\,^1S_0 - 5\,^3P_1$	3261	$2.5 \cdot 10^{-6}$
	$5\,^1S_0 - 5\,^1P_1$	2288	$2 \cdot 10^{-9}$
Zn	$4\,^1S_0 - 4\,^3P_1$	3076	$1 \cdot 10^{-5}$
	$4\,^1S_0 - 4\,^1P_1$	2139	$\ll 10^{-7}$
Na	$3\,^2S_{1/2} - 3\,^2P$	5896,5890	$1.5 \cdot 10^{-8}$

It should be noted that if the nature of the interacting particles are such that in the energy transfer a large amount of the energy will have to go into translational motion, i.e. kinetic energy, than the energy transfer will not occur(13).

I.e. the probability for a transfer of energy would be very small. Lately, wave-mechanics(14) has shown that if two atoms or molecules have energy levels lying near together a "quantum mechanical resonance" effect takes place between them. Thus for an activated sensitizer to give up its energy to a reactant the reactant must possess an energy level lying near the energy level of the activated sensitizer. The closer together the energy levels; the greater the "quantum mechanical resonance" or probability of energy transfer.

A good demonstration as to this effect was experimently given by Beutler and Josephy(15). They showed that, by exciting sodium vapor by the mercury resonance line 2537$\overset{o}{A}$, in the sensitized fluorescence received the Na line 3^2P- 9^2S or (4223, 4420) was by far the strongest line observable. This was accounted for by the fact that the difference in energy between the states $Na(9^2S)$ and $Hg(6^3P_1)$ is only 0.02 volts.

Two problems arise when one studies photosensitized reactions: 1, The quenching of the sensitizer and 2, the subsequent reactions.

It is thus appropriate to give a brief resume of the experimental work done on the quenching of mercury, cadmium and zinc resonance radiation.

After Wood's(11) initial discovery of the quenching of the 2537$\overset{o}{A}$ mercury resonance radiation, the most extensive early investigation of the quenching of 2537$\overset{o}{A}$ mercury resonance radiation was done by Stuart(16). He observed only slight quenching by the inert gases helium and argon, and nitrogen; this fact was shown to be due mainly to pressure broadening, in later work; whereas CO, O_2 and H_2 all quenched to a value of Q approximately equal to 0.4 at a pressure of 0.5 mm. of mercury,

$$\text{where} \quad Q = \frac{\text{Intensity of resonance radiation in presence of foreign gas.}}{\text{Intensity of resonance radiation without foreign gas.}}$$

The hydrogen being the most efficient and the carbon monoxide being the least efficient of the three quenchers.

Stuart's results are criticised because of the presence of Lorentz or pressure broadening and unaccountable diffusion of imprisoned radiation in the experiments.

Accordingly the later experiments of Zemansky(17) and of Bates(18) were made with apparatus and precautions such that the above criticisms were eliminated from their experiments. It was found that within a pressure range in which Lorentz broadening was negligible there was no appreciable quenching of mercury resonance radiation($2537\overset{o}{A}$) by helium or argon.

The following table gives a number of effective cross-sections calculated from their experimental results.

Table III

Gas	Effective cross-section times 10^{16} cm.^{2} .
CH_4	0.0852
N_2	0.274
C_2H_6	0.594
C_3H_8	2.32
C_4H_{10}	5.88
H_2	8.60

Steacie(19) made an investigation of the quenching of mercury resonance radiation($2537\overset{o}{A}$) by ethylene. A quenching cross-section of $48 \cdot 10^{-16}$ cm.^{2} was found; 0.4 mm. of C_2H_4 was necessary for a quenching of half-value.

Bates(20) made a qualitative study of the quenching of cadmium resonance radiation(3261Å) by hydrogen and showed that hydrogen was very effective in quenching the cadmium resonance radiation.

Bender(21) found that in the quenching of cadmium resonance radiation, the upperline(3261Å) was practically all quenched by 4 mm. of hydrogen, whereas there was no noticable quenching of the lower line(2288Å). Similar results were obtained with zinc, the upper line(3076Å) was quenched, whereas the lower line(2139Å) was not.

Lipson and Mitchell(22) have made a quantitative study of the quenching of the upper resonance line(3261Å) of cadmium. The results obtained are tabulated immediately below in table IV. The table lists the pressure of foreign gas required for a quenching of $1/2$ value, the respective slope of the line obtained by plotting $1/Q$ against the pressure of foreign gas in mm. and the cross-section.

The quenching collision cross-section, c_q^2, was determined as follows from the Stern-Volmer formula(23),

$$Q = \frac{1}{1 + tZ_q}$$, where Q= quenching,

Table IV

Gas	Pressure required for Q to $= 1/2$ in mm.	Slope, $1/Q \cdot P$ in mm.$^{-1}$	c_q^2 times 10^{16} cm.^{2}
H_2	0.4	2.45	0.67
D_2	1.5	0.50	0.19
NH_3	17	0.063	0.041
N_2	45	0.022	0.021
CH_4	60	0.016	0.012
CO	7	0.15	0.14

$t =$ life-time of the excited state,

$Z_q =$ the number of quenching collisions per sec. per cc. per excited atom,

and from the formula for Z_q calculated on the basis of the Maxwellian distribution of velocities,

i.e. $$Z_q = 2Nnc_q^2 \left[2\pi kT(1/M_1 + 1/M_2) \right]^{1/2} .$$

Combining the two formulae we get

$$c_q^2 = \frac{1/Q \cdot P}{2666.6t \left[2\pi N/kT(1/M_1 + 1/M_2) \right]^{1/2}} ,$$

where M_1 and M_2 are the molecular weights of the colliding particles, c_q^2 is the quenching cross-section, N is Avogadro's number,

K is the gas constant, t is the life time of the excited state, T the absolute temperature, and $1/Q \cdot P$ is the slope of the quenching line obtained by plotting $1/Q$ against P, the pressure in mm.

HYDROCARBON BOND STRENGTHS

Before dealing with the sensitized reactions of the hydrocarbons let us first consider the bond strengths found in these compounds.

The bonds and the commonly accepted values are:

Bond	Strength in kilo-cal.
C-H	95 ± 10
C-C	85 ± 10
C=C	145 ± 15
C≡C	200 ± 20
H-H	102.5

Note: The C-H bond in methame and possibly ethylene has an abnormally high value; and that the strength of the H-H bond is 102.5 kcal. from spectroscopic determination.

The spectroscopic determination of bond values in the simpler hydrocarbons is a future

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Note: For a convenient list of bond strengths and references see table 32 in " Photochemistry" by Rollefson and Burton.

possibility; while bond determination from atomic

heats and other thermal data awaits an accurate

determination of the heat of vaporization of carbon,

i.e. $C_s \rightarrow C_g - ?$,and heat of reaction of $C_g \rightarrow 2C$.

Comparing these bond strengths with the

energies available from the resonance states of

mercury, cadmium and zinc we find that the values

from the two sets are fortuitously interspaced,

i.e.

Energy in kil-cal.	Bond	Resonance state	Resonance state plus hydride heat of formation.
170			
160			− Hg($6\,^1P_1$)+Hy.
150		− Hg($6\,^1P_1$)	− Zn($4\,^1P_1$)+Hy.
140	− C=C		− Cd($5\,^1P_1$)+Hy.
130		− Zn($4\,^1P_1$)	
120		− Cd($5\,^1P_1$)	− Hg($6\,^3P_1$)+Hy.
110		− Hg($6\,^3P_1$)	− Zn($4\,^3P_1$)+Hy.
100	− H-H	− Hg($6\,^3P_0$)	− Cd($5\,^3P_1$)+Hy.
90	− C-H	− Zn($4\,^3P_1$)	
80	− C-C	− Cd($5\,^3P_1$)	
70			
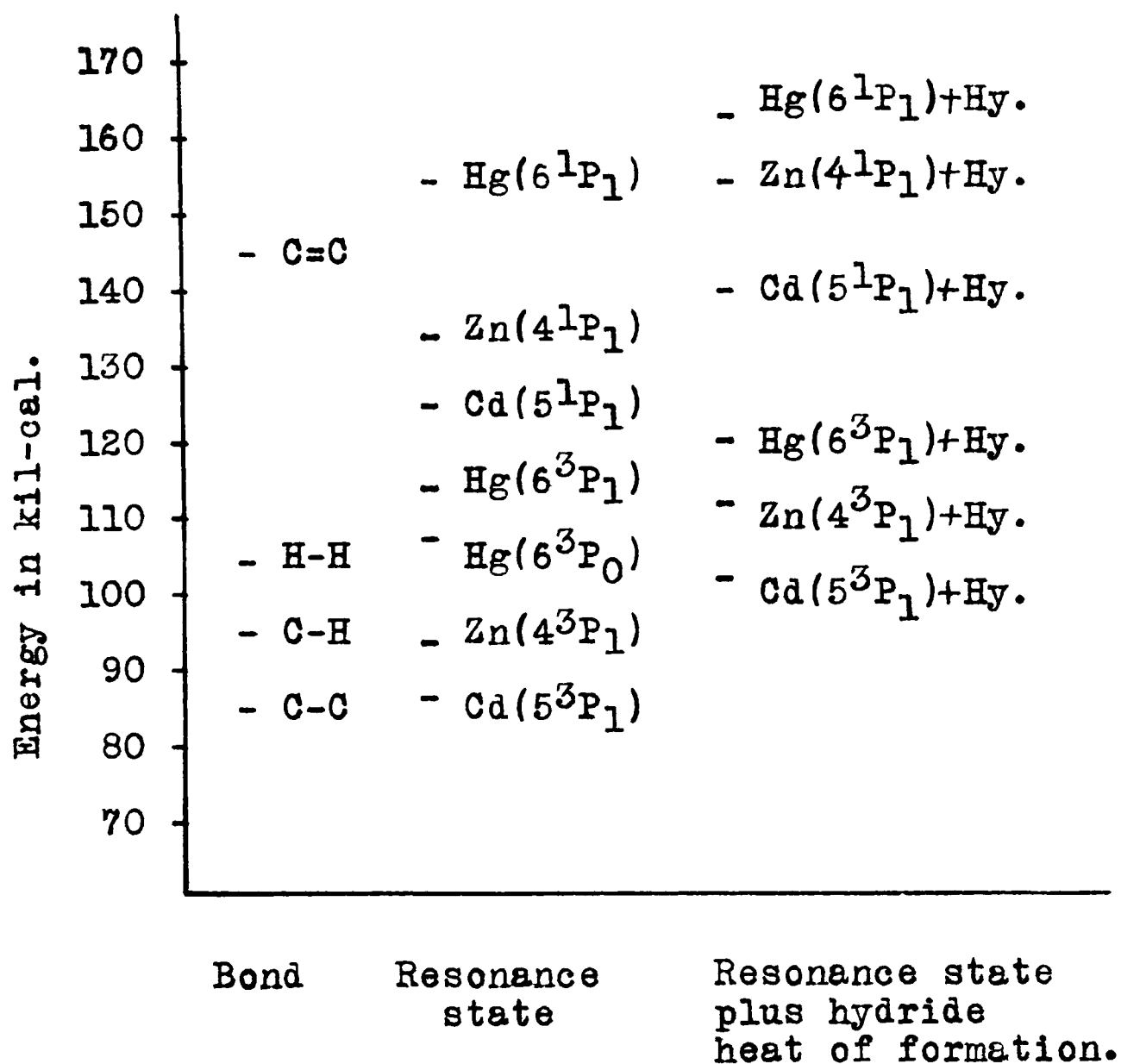
Energy Diagram.

Although the possibility of hydride formation may apparently complicate the photosensitized reaction of a hydrocarbon, on further thought it is seen that the formation of a hydride will probably only take place if " quantum mechanical resonance" is sufficient and energy conditions are satisfactory;

$$\text{e.g.} \quad M^* + HR \longrightarrow MH + R \pm \Delta \ ,$$
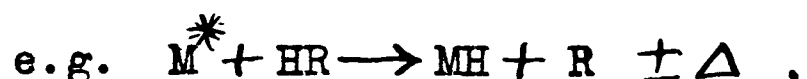
where Δ is the excess energy, which must be accomodated by MH and R or provided kinetically by the reactants. If Δ is inconveniently large the reaction will perhaps not go.

The sum of the heat of formation of the hydride and the energy in the activated state make another series of reference points on the energy diagram above.

, Yet if there should be a hydride formation, a C-H bond split or a formation of H_2 (and consequently $M^* + H_2 \longrightarrow MH + H$) in the primary reaction, than the secondary reactions in many cases would be that of atomic hydrogen; and the resulting products of the photosensitization would therefore be similar to those obtained by subjecting the same hydrocarbon to hydrogen atoms by means of the Wood-Bonhoeffer method, as often is the case. Sometimes mixtures of hydrogen and hydrocarbon are used in order to take advantage of this property of $M^* + H_2 \longrightarrow MH + H$ and thus investigate the H-atom reaction of the hydrocarbon.

Due to the "uncertainty principle" of Heisenberg,

$\Delta E \cdot t = h$, where E is the energy required to raise the sensitizer into the energy state of life-time t, and h is Plank's constant, there exists an uncertainty or haziness in an energy level of amount $\Delta E = h/t$. Consequently the shorter the life-time of the state the greater the uncertainty in E; and therefore the greater is the possibility of "quantum mechanical resonance", and resulting quenching and reaction if the energy transfered is sufficient.

On looking back at table II showing the life-times of the various states it is evident that in decreasing values of ΔE these states may be listed thus

$$Hg(6^1P_1) > Cd(5^1P_1) > Zn(4^1P_1) > Hg(6^3P_1)$$
$$> Cd(5^3P_1) > Zn(4^3P_1) .$$
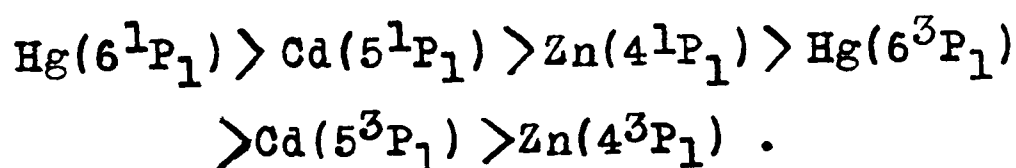
It should be noted that, although smaller life-time makes greater resonance possible, there is an opposing current to efficient quenching and that is the reverse of the following process

$$M + h\nu(\text{resonance}) \rightleftarrows M^*.$$
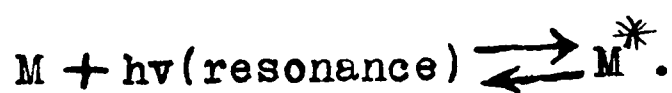
As life-time values approach in magnitude the time for traversing a mean free path, a shorter life-time gives less time for the deactivation of the sensitizer by collisions, i.e. a decrease in the probable quenching.

A more detailed consideration of energies, life-times, bond strengths etc. would not be justified from the point of view of both the amount and accuracy of the data accumulated concerning photosensitization.

THE PHOTOSENSITIZED AND H-ATOM REACTIONS OF THE HYDROCARBONS

Of the three metals mercury, cadmium and zinc, mercury is the easiest and most convenient to use for work in photosensitization, since at room temperatures it has a sufficient vapor pressure; whereas a temperature of $250^{\circ}C$. is necessary for cadmium and $350^{\circ}C$. for zinc.

Consequently there have been a considerable number of mercury photosensitized reactions studied, only a few with cadmium and none with zinc.

The following review and brief description of work and results on the photosensitization of the hydrocarbons is arranged thus:

1, The mercury sensitized reactions of,

    a, Hydrogen,
    b, Saturated hydrocarbons,
    c, Unsaturated hydrocarbons.

2, The cadmium sensitized reactions of,

    a, Hydrogen,
    b, Saturated hydrocarbons,
    c, Unsaturated hydrocarbons.

The equally important H-atom reactions of the respective hydrocarbon whether by the Wood-Bonhoeffer method or the $Hg(6^3P_1) + H_2$ method is discussed under the respective sensitized reaction where other pertinent data and conclusions are also included.

$$Hg + 2537\overset{o}{A} + H_2 \longrightarrow$$
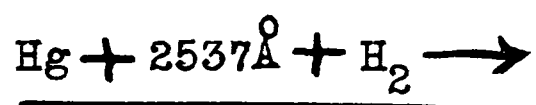
Cario and Franck(24) were the first to show that atoms excited by resonance radiation may give over their energy to other molecules and cause them to react. They found that hydrogen, activated by collision with excited mercury atoms, could be made to react with metallic oxides. They demonstrated the necessity of having both the unreversed $2537\overset{o}{A}$ line and the mercury vapor present before reaction will occur.

They concluded that the reaction is

$$Hg(6^1S_0) + 2537\overset{o}{A} \underset{(4.9 \text{ volts})}{\longrightarrow} Hg(6^3P_1)$$

and $Hg(6^3P_1) + H_2 \longrightarrow Hg(6^1S_0) + H + H + 0.4$ volts of
  $(4.9v.)$ $(\cong 4.5v.)$ energy in excess,
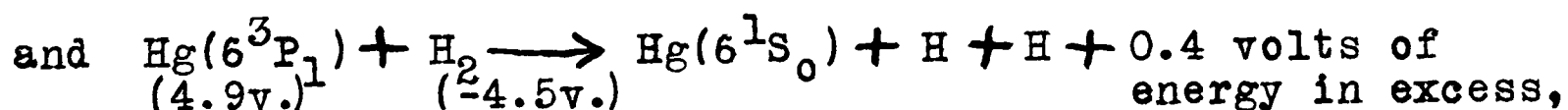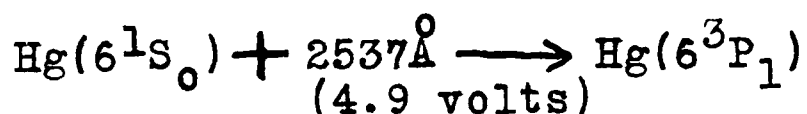
followed by $H + $ oxide $\longrightarrow$ free metal or change in oxide.

Senftleben(25) has demonstrated the formation of H atoms in $Hg + 2537\overset{o}{A} + H_2$ by a change in the heat conductivity of the H_2.

Meyer(26) has shown that H atoms are also formed by the $Hg(6^3P_0)$ state by the addition of N_2 which resulted in a marked increase of H production and a faster reduction of oxides.

Thus indicating that the following takes place

$$Hg(6^3P_1) + N_2 \longrightarrow Hg(6^3P_0) + N_2^{*}$$

and $Hg(6^3P_0) + H_2 \longrightarrow Hg(6^1S_0) + H + H$.
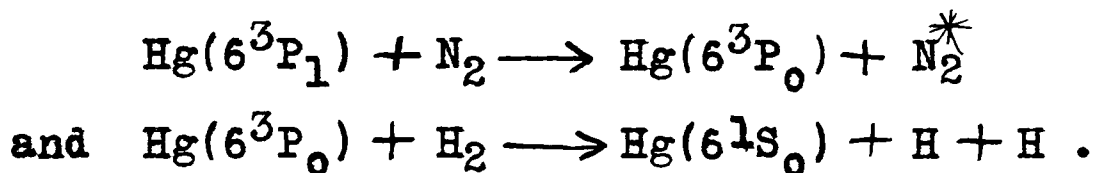
Thus by using N_2 in a system one can investigate reactions sensitized by the $Hg(6^3P_0)$ state; giving us another reference point on our energy level diagram.

But Compton and Turner(27) on obtaining HgH bands from a low voltage arc in hydrogen and mercury assumed that the reaction gave a hydride plus a hydrogen atom,

i.e. $Hg(6^3P_1) + H_2 \longrightarrow HgH + H$.
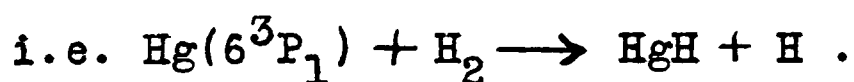
Gaviola and Wood(28) detected what was thought to be sensitized band fluorescence of HgH from a resonance cell containing a mixture of $Hg + 2537\overset{o}{A} + N_2 + H_2$.

But recently Olsen(29) has shown that the HgH was not in the normal state since he did not receive any HgH resonance.

The weak bands emitted were shown to be independent of the presence of HgH in the light source. He concluded that the weak bands observed belonged to the

$^2\pi_{1/2,3/2} \longrightarrow {}^3\Sigma_{1/2}$ system, and that atomic H was necessary for the formation of the activated hydride,

$$Hg(6^3P_1) + H \longrightarrow HgH(^2\pi_{1/2,3/2}) \ .$$
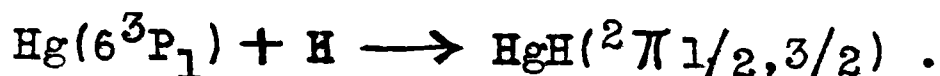
It may be that the hydride is not formed; but there has to be more evidence before a definite conclusion can be drawn. For the absence of band resonance radiation does not definitely prove the absence of HgH in the reaction, because the HgH formed may possess an energy of 0.62 volts above normal and could be in a position where no resonance radiation or only a very little at one end of the band would be absorbed.

$$Hg + 2537\overset{o}{A} + CH_4 \longrightarrow$$
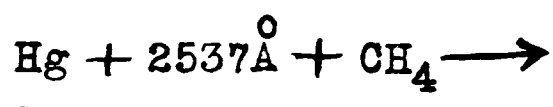
From thermal, photochemical, H-atomic reaction and mercury photosensitization data available it has been concluded that the C-H bond strength in methane is higher than in other paraffins.

Early investigations(30,31,32,) of $Hg + 2537\overset{o}{A} + CH_4$ reported no reaction.

It has since been shown, by Morikawa, Benedict and Taylor(33) that a little reaction takes place, while Steacie and Phillips(34) found that H_2 was produced in a circulatory system.

Presumably the primary equation is

$$Hg(6^3P_1) + CH_4 \longrightarrow CH_3 + H + Hg(6^1S_0) .$$

The quantum yield is very low, 0.04 or less, suggesting that of what little quenching there is most of it is by
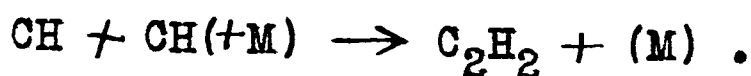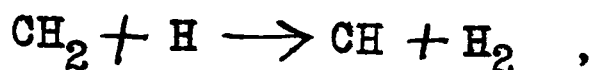
$$Hg(6^3P_1) + CH_4 \longrightarrow Hg(6^3P_0) + CH_4^* .$$
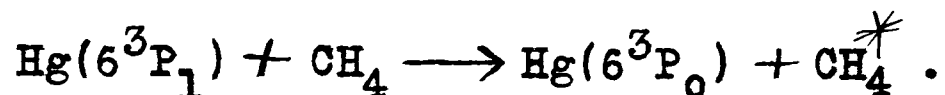
The photochemical decomposition of methane necessitates a light source emitting wave lengths below 1800$\overset{o}{A}$, since methane is transparent to radiation of longer wave length than this.

The hydrogen lamp through fluorite used by Leighton and Steiner(35) and the Harteck xenon lamp used by Groth and Laudenklos(36) on methane gave results which were in good agreement.

Groth and Laudenklos found that the reaction products were chiefly hydrogen and acetylene with smaller amounts of ethane, ethylene, and higher hydrocarbons.

The mechanism which was most compatible to products and quantum yields was the following, primary reaction, $CH_4 + h\nu \longrightarrow CH_3 + H$, and the secondary reactions,

$$CH_3 + H(+M) \longrightarrow CH_4 + (M) ,$$

$$CH_3 + CH_3(+M) \longrightarrow C_2H_6 + (M) ,$$

$$CH_3 + CH_3 \longrightarrow C_2H_4 + H_2 ,$$

$$CH_3 + H \longrightarrow CH_2 + H_2 ,$$

$$H + H(+M) \longrightarrow H_2 + (M) ? ,$$

$$CH_2 + CH_2(+M) \longrightarrow C_2H_4 + (M) ,$$

$$CH_2 + CH_2 \longrightarrow C_2H_2 + H_2 ,$$

$$CH_2 + H \longrightarrow CH + H_2 \quad ,$$

$$CH + CH(+M) \longrightarrow C_2H_2 + (M) \quad .$$
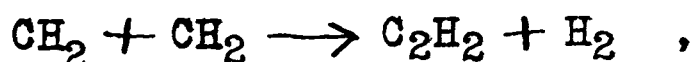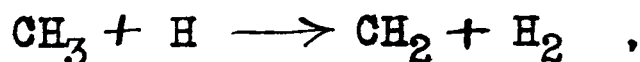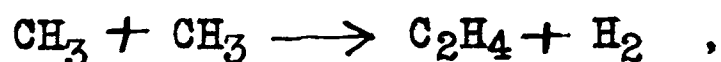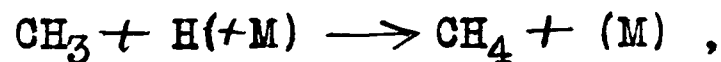
But the small amounts of C_2H_4 and C_2H_6 formed as compared with the large amounts of C_2H_2 and especially H_2 could be explained to a certain extent thus,

$$C_2H_6 + h\nu \longrightarrow C_2H_4 + H_2 \quad , \text{ and}$$

$$C_2H_4 + h\nu \longrightarrow C_2H_2 + H_2 \quad .$$
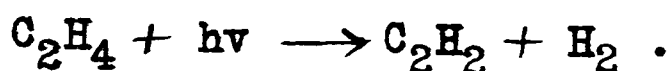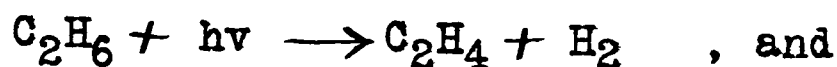
The other primary reaction suggested for the CH_4 decomposition is $CH_4 + h\nu \longrightarrow CH_2 + H_2$.

Both primary reactions have been suggested at different times by various authors as the initial reaction in the thermal decomposition of CH_4 .

$$\underline{Hg + 2537\overset{o}{A} + H_2 + CH_4 \longrightarrow}$$
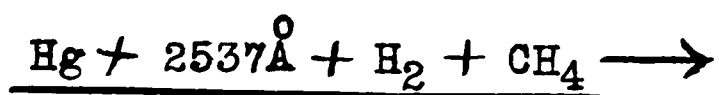
This reaction is apparently the same as the H-atom reaction of CH_4 by the W.-B. method in which the products are the same as the reactants. For the primary reaction here is the production of H atoms by the decomposition of the H_2 by the $Hg(6^3P_1)$.

Although there is still much debate concerning the H-atom reaction of methane, the main body of evidence indicates that the following reaction, employed by Trenner, Morikawa and Taylor in a C-H bond strength calculation in methane, is the right one.

I.e. $H + CH_4 \underset{k_2}{\overset{k_1}{\rightleftarrows}} CH_3 + H_2$, where the energy of
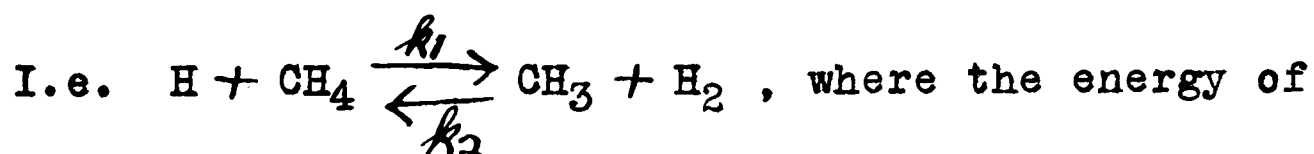
activation of the reaction 'k_1' is 13 kcal. and for the reverse reaction 'k_2' the activation energy is 9 kcal. It follows, therefore, that the reaction as written is approximately 4 kcal. endothermic. Hence since

$$H_2 \longrightarrow 2H \quad -102.5 \text{ kcal.} \quad , \quad \text{we have}$$
$$CH_4 \longrightarrow CH_3 + H \quad -106.5 \text{ kcal.}$$
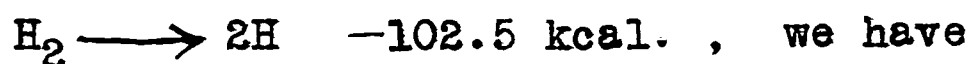
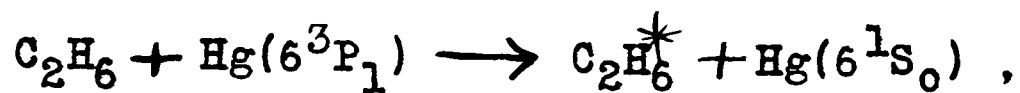In other words the C-H bond strength in methane is about 106.5 kcal.

The energy of activation of reaction 'k_1' is calculated from data obtained from the H-atom reaction of methane by the W.-B. method. While the energy of activation of reaction 'k_2' is deduced by a method such as the photolysis of mercury di-methyl alone and in the presence of hydrogen, as was done by Taylor and Cunningham(85).

$$Hg + 2537\overset{o}{A} + C_2H_6 \longrightarrow$$
and
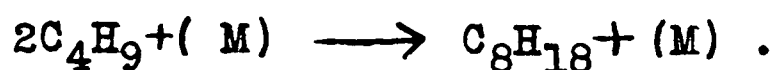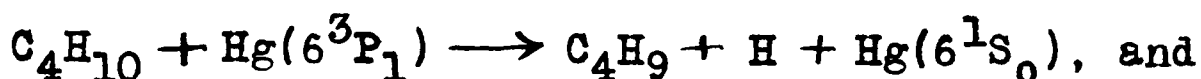$$Hg + 2537\overset{o}{A} + C_2H_6 + H_2 \longrightarrow$$
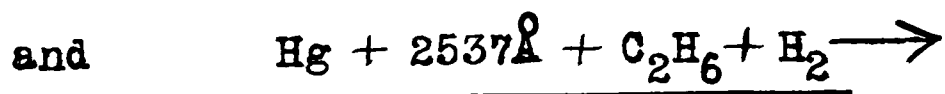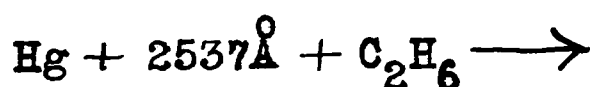
These mercury photosensitizations were first studied by H.S. Taylor and his collaborators in the course of their classical investigations of mercury photosensitized reactions. They(38) showed that ethane is attacked by excited mercury atoms and, if hydrogen was present, by hydrogen atoms also.

A more than qualitative investigation of the plain reaction was made by Kemula, Mrazek and Tolloczko(39). They found hydrogen, methane, butane and octane with a small amount of hexanes as main products.

The reaction mechanism which they suggest is

$$C_2H_6 + Hg(6^3P_1) \longrightarrow C_2H_6^* + Hg(6^1S_0) ,$$
$$C_2H_6^* \longrightarrow C_2H_5 + H ,$$
$$2C_2H_5 + M \longrightarrow C_4H_{10} + M ,$$
$$2H + M \longrightarrow H_2 + M$$
$$C_2H_6 + H \longrightarrow C_2H_5 + H_2 ,$$
$$C_2H_6 + H \longrightarrow CH_3 + CH_4 .$$
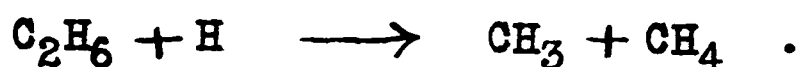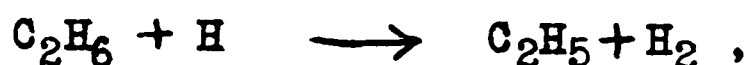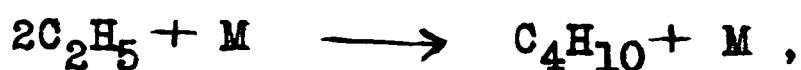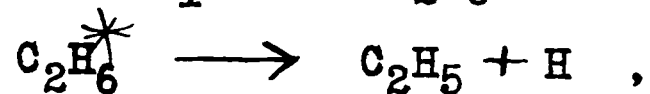
And the fact that octane is the chief higher product suggests that the chéif reaction of butane is

$$C_4H_{10} + Hg(6^3P_1) \longrightarrow C_4H_9 + H + Hg(6^1S_0), \text{ and}$$
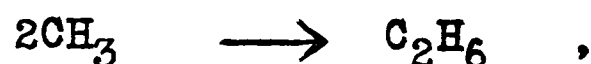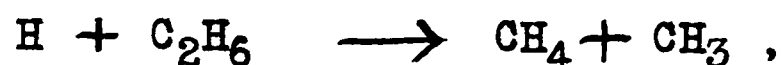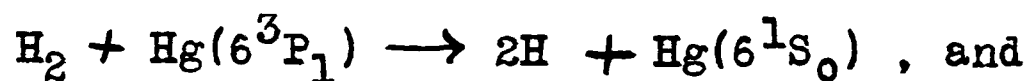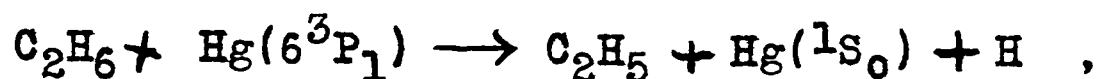$$2C_4H_9 + (M) \longrightarrow C_8H_{18} + (M) .$$

But Steacie and Phillips(40) by an efficient trapping out of the butane in a circulating system received products which consisted exclusively of methane, propane and butane, and in a continuous flow system got the same in addition to considerable hydrogen. Thus definitely showing that the hexane and octane received by Kemula, Mrazek and Tolloczko were due to the photosensitized secondary reactions of propane and butane.

In the circulating system(Steacie and Phillips) the reaction with added hydrogen gave the same products; the

% of methane formed being quite a bit higher, and hydrogen was consumed.

They concluded that the mechanism or processes occuring, both with and without added hydrogen, are,

$$C_2H_6 + Hg(6^3P_1) \longrightarrow C_2H_5 + Hg(^1S_0) + H \quad,$$

$$H_2 + Hg(6^3P_1) \longrightarrow 2H + Hg(6^1S_0) \quad, \text{ and}$$

$$H + C_2H_6 \longrightarrow C_2H_5 + H_2 \quad,$$

$$H + C_2H_6 \longrightarrow CH_4 + CH_3 \quad,$$

$$2CH_3 \longrightarrow C_2H_6 \quad,$$

$$CH_3 + C_2H_5 \longrightarrow C_3H_8 \quad,$$

$$2C_2H_5 \longrightarrow C_4H_{10} \quad,$$

$$2H \longrightarrow H_2 \quad, \text{ and}$$

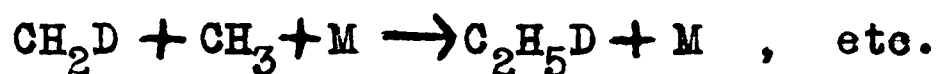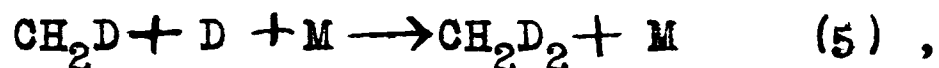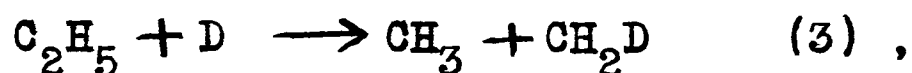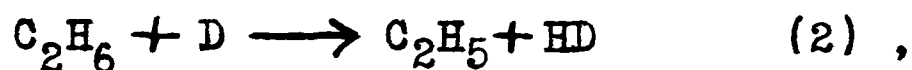$$H + C_2H_5 \longrightarrow 2CH_3 \quad \text{could also be included.}$$
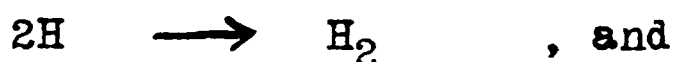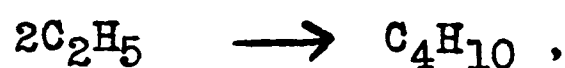
The H-atom reaction(W.-B.method),with ethane only, yields methane (Trenner, Morikawa and Taylor(37)). They concluded that at room temperature the main reaction using deuterium is

$$D + C_2H_6 \longrightarrow CDH_3 + CH_3 \quad, \tag{1}$$
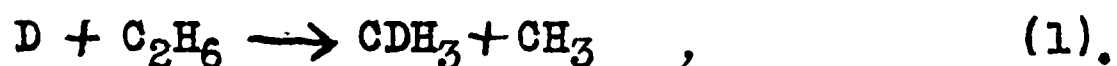
Steacie(41) confirmed methane as the sole product. His activation energy of 6.4 kcal. for the reaction is in good agreement with the 7.2 kcal. for the same found by Trenner, Morikawa and Taylor.

But Gorin,Kauzman,Walter and Eyring(42) by semi-empirical methods calculated that such a reaction should have an activation energy in the neighbourhood of 30 kcal.

Rice and Teller have, therefore, suggested the following mechanism, which fits the experimental results better than reaction (1), (Rice and Teller(43),also Taylor(92))

$$C_2H_6 + D \longrightarrow C_2H_5 + HD \qquad (2) ,$$

$$C_2H_5 + D \longrightarrow CH_3 + CH_2D \qquad (3) ,$$

$$CH_3 + D + M \longrightarrow CH_2D_2 + M \qquad (4) ,$$

$$CH_2D + D + M \longrightarrow CH_2D_2 + M \qquad (5) ,$$

$$CH_2D + CH_3 + M \longrightarrow C_2H_5D + M \qquad , \quad \text{etc.}$$

Reaction (2), followed by (3), we call the atomic cracking reactions and are responsible for the methane formed by (4) and (5). This type of reaction has been given strong support by Steacie and his co-workers in experiments of propane and butane with H atoms by the W.-B. method (44,45).

Note: The energy of activation of 6.8 kcal. accordingly applies to reaction(2) of the above scheme.

The reverse reaction

$$H_2 + C_2H_5 \longrightarrow C_2H_6 + H \qquad \text{has been assigned}$$

an energy of activation of 9 kcal. by Taylor and Moore(86), who arrived at this result through the decomposition of mercury and zinc di-ethyl alone and in the presence of H_2.

This gives us a value of 100.3 kcal. for the C-H bond in ethane, i.e. 100 ± 5 since the activation/values are not as accurate as written.

$$Hg + 2537\overset{o}{A} + C_3H_8 \longrightarrow$$

and
$$\underline{Hg + 2537\overset{o}{A} + C_3H_8 + H_2 \longrightarrow}$$
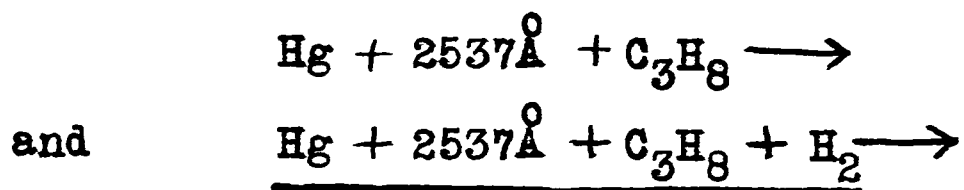
These reactions were investigated by Steacie and Dewar(46). They found that from $240^{\circ}C.$ to $323^{\circ}C.$ the products of the reaction, both with propane alone and with propane hydrogen mixtures, were almost exclusively hydrogen and hexanes (mainly 2,3-di-me-butane and 2 me-pentane).

There appears to be no doubt that with propane alone the primary step is

$$C_3H_8 + Hg(6^3P_1) \longrightarrow C_3H_7 + H + Hg(6^1S_0) \ .$$
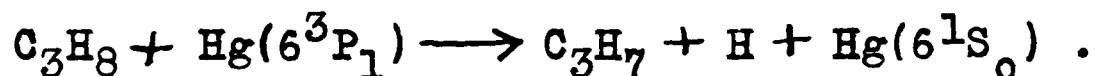
In the presence of hydrogen, on account of its very high quenching efficiency, almost all the excited mercury atoms will transfer their energy to hydrogen, and the primary step will be

$$H_2 + Hg(6^3P_1) \longrightarrow 2H + Hg(6^1S_0) \ .$$
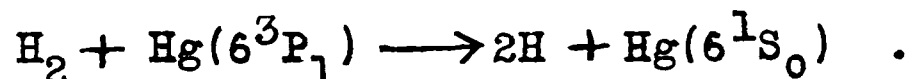
The principle secondary reactions are apparently in both cases

$$2C_3H_7 \longrightarrow C_6H_{14} \quad ,$$
$$2H \longrightarrow H_2 \quad , \text{ and}$$
$$H + C_3H_8 \longrightarrow C_3H_7 + H_2 \quad .$$
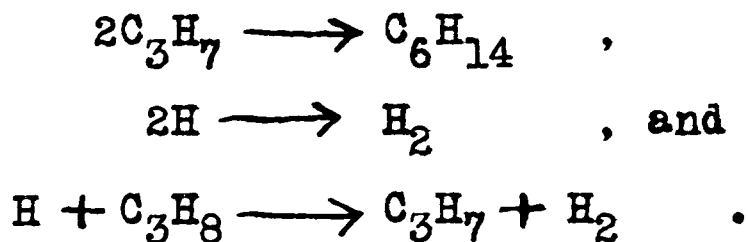
Taylor and Hill(38) showed that propane reacts slower with H atoms than does butane but faster than ethane by mercury photosensitization.

The first work reported on the H-atom reaction with propane by the W.-B.m. was by Trenner, Morikawa and Taylor(37), who reported that much more methane was formed than ethane especially at low temperatures.

Steacie and Parlee(44) made a thorough investigation of the H-atom reaction of propane over the temperature range $30^{\circ}C.$ to $250^{\circ}C.$ The products found were solely methane at low temperatures and methane, ethane and ethylene at high temperatures.

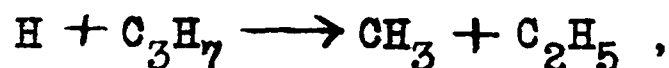They concluded that the results only can be explained on the assumption that the reaction

$$H + C_2H_5 \longrightarrow 2CH_3 \qquad \text{is of importance.}$$

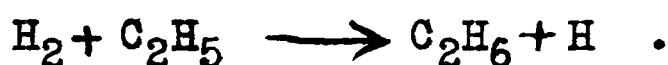The activation energy of the reaction, $H + C_3H_8 \longrightarrow$, is 10 ± 2 kcal.

The main steps in the postulated mechanism are:

Primary reaction $H + C_3H_8 \longrightarrow C_3H_7 + H_2$.
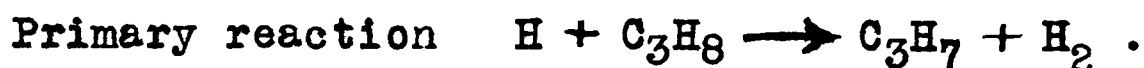
Secondary reactions at low temperatures

$$H + C_3H_7 \longrightarrow CH_3 + C_2H_5 ,$$
$$H + C_2H_5 \longrightarrow 2CH_3 ,$$
$$H + CH_3 \longrightarrow CH_4 .$$

Additional secondary reactions at high temperatures

$$C_3H_7 \longrightarrow C_2H_4 + CH_3 ,$$
$$2CH_3 \longrightarrow C_2H_6 ,$$
$$H + C_2H_5 \longrightarrow C_2H_6 ,$$
$$H + C_2H_4 \longrightarrow C_2H_5 , \text{ and}$$
$$H_2 + C_2H_5 \longrightarrow C_2H_6 + H .$$
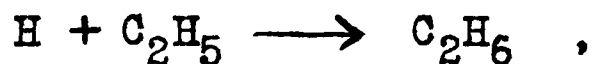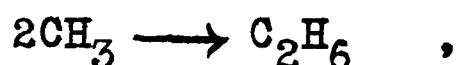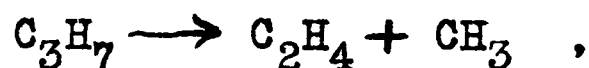
They also investigated the reactions of deuterium atoms with propane. It was found that the methane and ethane produced were highly deuterized, while the propane was not appreciably exchanged.

$$\underline{Hg + 2537\overset{o}{A} + C_4H_{10} \longrightarrow}$$
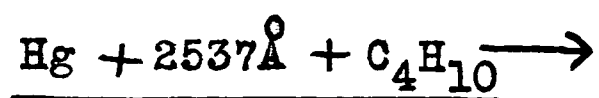
Steacie and Phillips(40) made one run on this reaction. They found that hydrogen and higher hydrocarbons were produced in large amounts. The quantum yield was roughly 0.55 .

The reaction at present is under investigation by Winkler and Hay(47); preliminary results show that hydrogen and heavy hydrocarbons chiefly octanes are the main products.

The apparent mechanism is

$$Hg(6^3P_1) + C_4H_{10} \longrightarrow C_4H_9 + H + Hg(6^1S_0) \ ,$$
$$2C_4H_9 \longrightarrow C_8H_{18} \ , \ and$$
$$2H \longrightarrow H_2 \ .$$

Trenner, Morikawa and Taylor(37) made one run on the H-atom reaction of butane by the W.-B.m. at 110^oC. and found that methane with some ethane and propane were formed.

A thorough investigation was carried out by Steacie and Brown(45) over a temperature range of 35^oC. to 250^oC. The activation energy is 9 $\pm$2 kcal.

The products consist solely of methane at low temperatures; at high temperatures ethane is also formed.

They concluded that the **results** indicate a mechanism in which a series of "atomic cracking" reactions play the main role. The main steps in the postulated mechanism are:

Primary process $H + C_4H_{10} \longrightarrow C_4H_9 + H_2$.
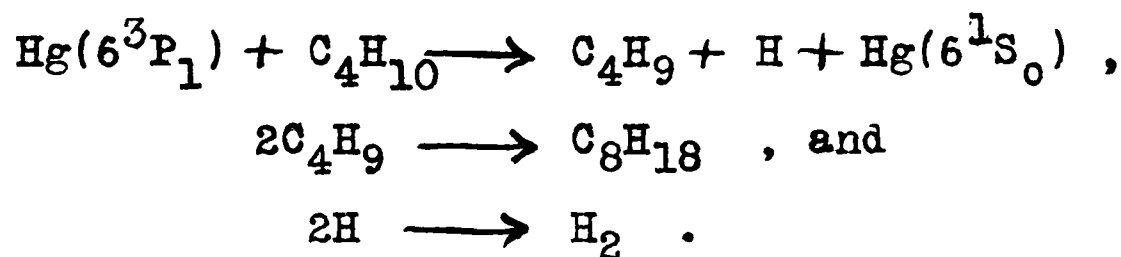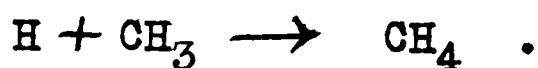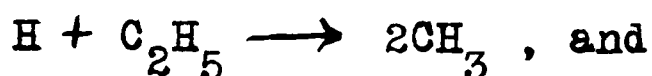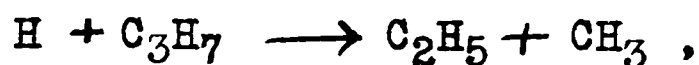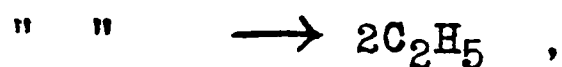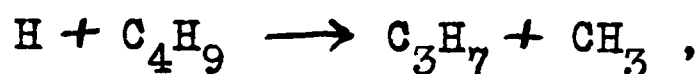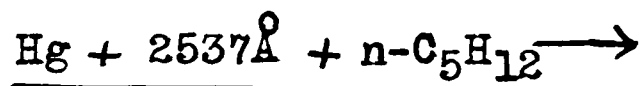
Secondary processes at low temperatures

$$H + C_4H_9 \longrightarrow C_3H_7 + CH_3 ,$$
$$\text{" "} \longrightarrow 2C_2H_5 ,$$
$$H + C_3H_7 \longrightarrow C_2H_5 + CH_3 ,$$
$$H + C_2H_5 \longrightarrow 2CH_3 , \text{ and}$$
$$H + CH_3 \longrightarrow CH_4 .$$

Additional secondary processes at higher temperatures

$$C_4H_9 \longrightarrow C_2H_4 + C_2H_5 ,$$
$$H + C_2H_4 \longrightarrow C_2H_5 ,$$
$$C_3H_7 \longrightarrow C_2H_4 + CH_3 ,$$
$$H_2 + C_2H_5 \longrightarrow C_2H_6 + H , \text{ and}$$
$$H_2 + CH_3 \longrightarrow CH_4 + H .$$

$$\underline{Hg + 2537\mathring{A} + n\text{-}C_5H_{12} \longrightarrow}$$
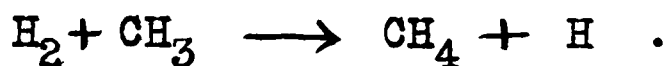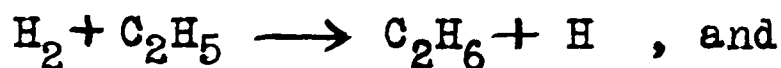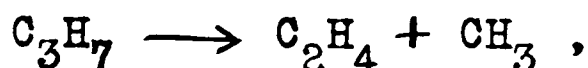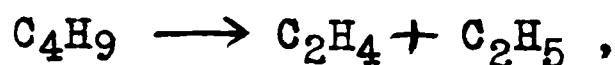
This reaction was investigated by Klemenc and Patat(48). They found that decomposition and polymerization both occured, hydrogen, methane and other hydrocarbons being formed. Similar results were obtained by Frankenburger and

Zell(49), who concluded that the primary process must involve both C-H and C-C bond splitting.

$$Hg + 2573\overset{o}{A} + n\text{-}C_6H_{14} \longrightarrow$$
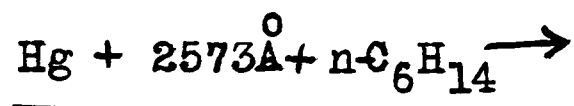
Taylor and Bates(50) made a brief investigation of this reaction. They reported production of much hydrogen and some methane.

$$Hg + 2537\overset{o}{A} + C_2H_4 \longrightarrow$$

The first investigation of this kind was made by Berthelot and Gaudechon(51), who found that an oily polymer was formed. L andau(52) found the same on exposing ethylene plus mercury vapor to a mercury arc.
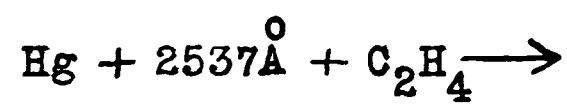
The first quantitative measurements were made by Taylor and Bates(50,53) using a cooled mercury arc.

They found that polymerization occured, together with the formation of acetylene, hydrogen and some methane.

The suggested mechanism is:

Primary process $Hg(6^3P_1) + C_2H_4 \longrightarrow C_2H_2 + H_2 + Hg(6^1S_0)$.

Secondary process $Hg(6^3P_1) + H_2 \longrightarrow 2H + Hg(6^1S_0)$,

$$H + C_2H_4 \longrightarrow C_2H_5 \text{ , and}$$

$$C_2H_5 + C_2H_4 \longrightarrow C_4H_9 \text{ , etc.}$$
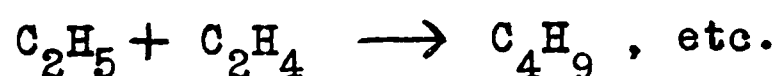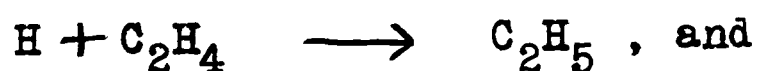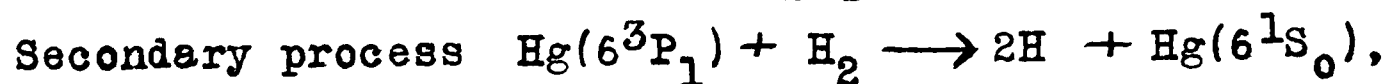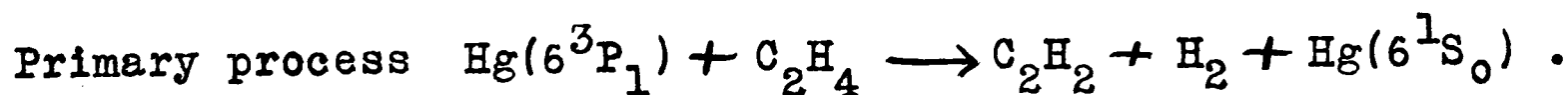
Olson and Meyers(54), Taylor and Hill(38) and Melville(55) similarly investigated the reaction and adopted the above primary step of acetylene formation.

A characteristic feature of the reaction is the initial pressure rise, presumably due to $C_2H_4 \longrightarrow C_2H_2 + H_2$.

The reaction and pressure rise is at present under investigation by Steacie and LeRoy(56), who confirm this pressure rise; the duration of which depends upon the intensity of light used. The initial pressure rise seems to be proportional to the amount of C_2H_2 formed.

Mooney and Ludlam(57) observed that when C_2H_4 is illuminated by the Al line 1860Å acetylene is formed; they showed that ethylene does not absorb appreciably until 2130Å is reached in the ultra-violet.

McDonald and Norrish(58) subjected C_2H_4 to a hydrogen lamp in a fluorite apparatus; products were hydrogen a polymer and a condensible gas.

Spectroscopic observation(59,60,61) indicates that the primary process is

$$C_2H_4 + h\nu \longrightarrow 2CH_2$$, and that the products arise in main from reactions involving CH_2 .

McDonald and Norrish also showed that by subjecting C_2H_2 to the same wave length the C_2H_2 could not account for the polymerization received in the C_2H_4 reaction.

Thermal investigations of C_2H_4, by various authors, have brought forth the following primary reactions etc.:

$$2C_2H_4 \longrightarrow CH_3CH_2CH=CH_2 \text{ , } (62),(63) .$$

$$2C_2H_4 \longrightarrow C_4H_8 \text{ , and}$$

$$C_2H_4 + C_4H_8 \longrightarrow C_6H_{12} \text{ , etc.} \qquad (64,65) \text{ .}$$

$$2C_2H_4 \longrightarrow C_4H_8 \text{ ,}$$

$$C_2H_4 \longrightarrow C_2H_2 + H_2 \text{ etc.} \qquad (66) \text{ .}$$

$$C_2H_4 \longrightarrow 2CH_2 \text{ ,}$$

$$CH_2 + C_2H_4 \longrightarrow C_3H_6 \text{ ,}$$

$$CH_2 + C_3H_6 \longrightarrow C_4H_8 \text{ , and}$$

$$CH_2 \longrightarrow CH + H \text{ , then}$$

$$2CH \longrightarrow C_2H_2 \qquad \text{etc.} \qquad (67) \text{ .}$$
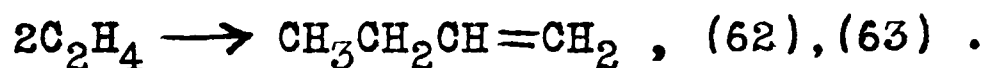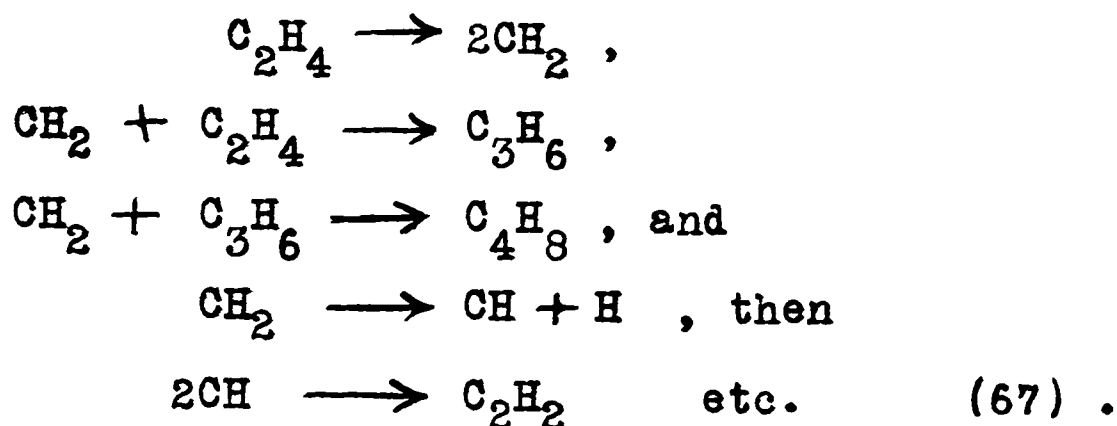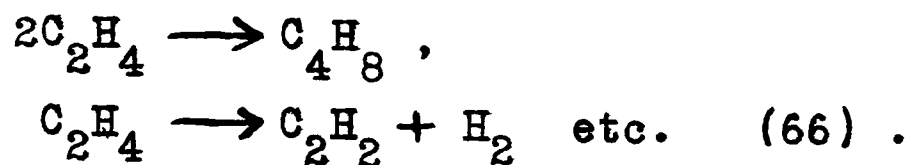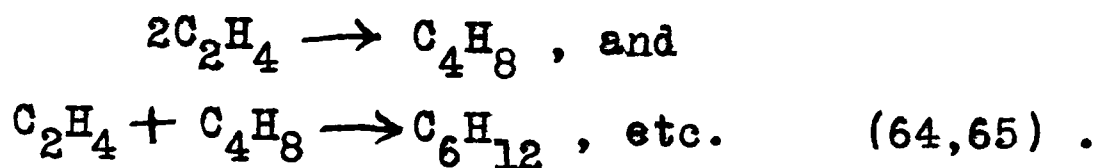
EVIDENCE FOR FREE RADICALS (CH_3 & CH_2)

Paneth and Hofeditz(1) showed the existence of CH_3 in the decomposition of organic compounds by its reaction with a lead mirror.

Rice and his co-workers with a somewhat similar method detected CH_3 in the decomposition products of hydrocarbons(68). But his attempts to detect CH_2 in hydrocarbon decomposition products were negative.

Whereas Belchetz and Rideal(69) using a hot platinum filament and an iodine mirror for a target from methane got CH_2I_2, and using a tellurium mirror and a carbon filament got telluroformaldehyde $(HCHTe)_n$. They repeated this with propane and butane(70) .

Rice and Glasebrook(71) showed the existence of CH_2 in the decomposition of diazomethane below 500°C. in a current of ether, receiving a telluroformaldehyde polymer of $(HCHTe)_n$. They later questioned the accuracy of this fact .

But Pearson, Purcell and Saigh(72) investigated the thermal and photochemical decomposition of ketene and diazomethane using the mirror technique. Their work appears to be quite conclusive.

They found that CH_2 was surprisingly stable in the presence of ketene, but not with diazomethane, the substances from which it was prepared.

I.e. $CH_2 = C = 0 \longrightarrow CH_2 + CO$, and

$CH_2N_2 \longrightarrow CH_2 + N_2$, where the reaction $2CH_2 \longrightarrow C_2H_4$ is slow, the half life of the radical being of the order of 0.2 sec. in ketene; but the reaction $CH_2 + CH_2N_2 \longrightarrow C_2H_4 + N_2$ is fast, and accordingly the half life of methylene in diazomethane is of the order of 0.005 sec.

They find that methane has little effect on the life of the methylene radical and hence the reaction

$CH_2 + CH_4 \longrightarrow C_2H_2$ or $2CH_3$ is slow at room temperatures.

They conclude that CH_2 is a molecule with a bivalent carbon rather than a radical with two free valencies .

$$Hg + 2537\overset{o}{A} + C_2H_4 + H_2 \longrightarrow$$
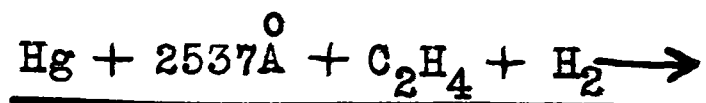
Was first investigated in a qualitative way by Taylor and Marshall(73). They found a pressure decrease, presumably owing to the formation of ethane .

Taylor and Hill(38) showed that when H_2 was in large excess in the reaction, than the products were practically all ethane; but with relatively more C_2H_4 higher hydrocarbons were formed with also a little methane.

Melville(74) compared the reactions of ethylene with hydrogen and deuterium atoms. He found no detectable difference in rate and therefore concluded that the rate controlling step must be a hydrogen or a deuterium atom reaction, otherwise the difference in zero point energies would make itself felt.

Olson and Meyers(75) also investigated the reaction and found that ethane was the main product and that the greater the ratio C_2H_4/H_2 the more propane and butane formed.

The first H-atom reaction of C_2H_4 by the W.-B.m. was carried out by Wartenberg and Schultze(76). They found the reaction rapid yielding principally ethane, with a little acetylene.

Gieb and Harteck(77) found that ethane was also formed when ethylene and hydrogen atoms were brought together at liquid air temperatures. This points to an energy of activation of around 5 kcal. for the reaction

$$H + C_2H_4 \longrightarrow C_2H_5 \ .$$

Recently Jungers and Taylor[78] have made a careful investigation of the reaction $C_2H_4 + H_2 + Hg + 2537\overset{o}{A} \longrightarrow$. They found that in a clean vessel which was flamed before each run to remove a layer of polymer, $(CH_2)_n$, from the wall, the reaction gave almost exclusively butane as a product.

They concluded that the mechanism is

$$Hg(6^3P_1) + H_2 \longrightarrow Hg(6^1S_0) + 2H \ ,$$
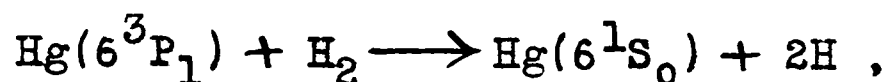
$$H + C_2H_4 \longrightarrow C_2H_5 \ , \text{ very fast; since this}$$

is fast, the H-atoms are swept up as fast as formed leaving the main possible reaction for the C_2H_5 radical to do is that of combining with itself,

$$\text{i.e. } 2C_2H_5 \longrightarrow C_4H_{10} \ . \quad \text{For very little ethane}$$

is formed, hence they conclude that the reaction

$$H_2 + C_2H_5 \longrightarrow C_2H_6 + H \quad \text{is slow under these}$$

conditions as must also be the reaction

$$C_2H_5 + C_2H_4 \longrightarrow C_4H_9 \ .$$
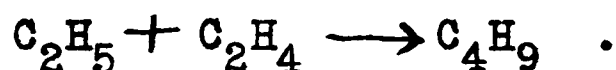
In fact what ethane is formed probably comes from the disproportionation reaction

$$2C_2H_5 \longrightarrow C_2H_4 + C_2H_6 \ .$$

$$Hg + 2537\overset{o}{A} + C_3H_6 + H_2 \longrightarrow$$
$$Hg + 2537\overset{o}{A} + C_4H_8 + H_2 \longrightarrow$$
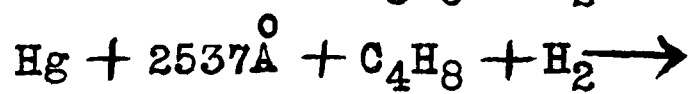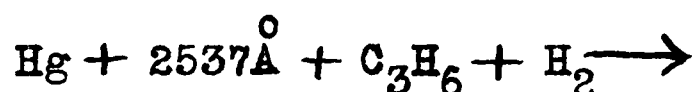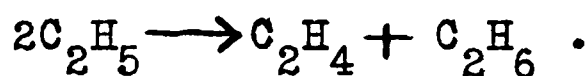
These reactions were briefly investigated by Moore and Taylor[79].

The main products obtained were for

	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_8H_{18}	In
PROPYLENE:	2	1	26	5	2	64	-	% ,and
n-BUTYLENE:	3	1	1	29	-	-	66	% .

The results indicate that the mechanism for both reactions are the same, using propylene as example we have the following secondary steps

$$H + C_3H_6 \longrightarrow C_3H_7 \quad , \tag{1}$$

$$2C_3H_7 \longrightarrow C_6H_{14} \quad , \tag{2}$$

$$H + C_3H_7 \longrightarrow C_3H_8 \quad , \text{ or} \tag{3}$$

$$2C_3H_7 \longrightarrow C_3H_6 + C_3H_8 \quad . \tag{4}$$
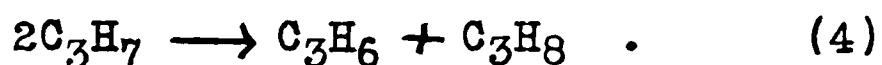
Thus indications are that reaction(1) has a low energy of activation, as in the case with the analogous reaction of ethylene; and more propane is formed from propylene than ethane from ethylene, this may be due to a greater importance of reaction(4) .

CADMIUM PHOTOSENSITIZED REACTIONS

$$Cd + 3261 \overset{o}{A} + H_2 \longrightarrow$$

$$Cd + 2288 \overset{o}{A} + H_2 \longrightarrow$$
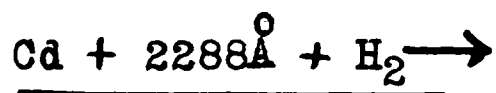
Reaction $Cd(5^3P_1) + H_2 \longrightarrow CdH + H$ undoubtedly goes since Bender(21) demonstrated both the quenching of $3261\overset{o}{A}$ resonance radiation by hydrogen and the emission of CdH bands from the resonance cell.

$$Cd(5^1P_1) + H_2 \rightarrow \text{ does not go(?) since Bender(21)}$$

detected no quenching by the H_2 .

$$Cd + 3261\overset{o}{A} + CH_4 \rightarrow$$
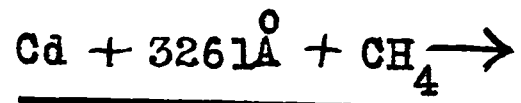
Has not as yet been investigated. If a reaction
has not been included in this summary than it has not been
studied as yet.

$$Cd + 3261\overset{o}{A} + C_2H_6 \rightarrow$$
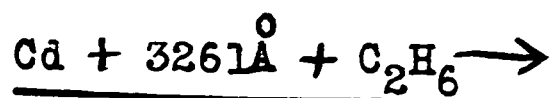
This reaction has been investigated quite thorough-
ly by Steacie and Potvin(80). The products of the reaction
are hydrogen, methane, propane, butane and higher hydrocarbons.

They concluded that the primary process is a C-H
bond split, probably by the reaction

$$Cd(5^3P_1) + C_2H_6 \longrightarrow CdH + C_2H_5 .$$
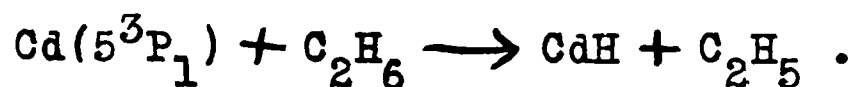
The methane resulting from methyl radicals produced by

$$H + C_2H_5 \longrightarrow 2CH_3 \qquad , \text{ and the higher}$$

hydrocarbons from recombination reactions of the radicals.

$$Cd + 3261\overset{o}{A} + C_2H_6 + H_2 \rightarrow$$
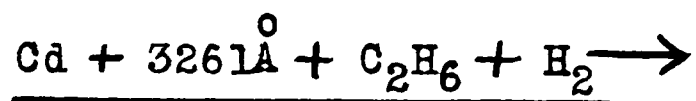
Also was investigated by Steacie and Potvin(80).
The chief products were methane, propane and butane plus
some hydrogen and higher hydrocarbons.

Here the primary reaction is most likely to be mainly

$$Cd(5^3P_1) + H_2 \longrightarrow CdH + H \text{ , followed}$$

by
$$H + C_2H_6 \longrightarrow C_2H_5 + H_2 \text{ , and}$$

$$H + C_2H_5 \longrightarrow 2CH_3 \quad \text{; and then various}$$

recombinations follow.

$$Cd + 3261\overset{o}{A} + C_3H_8 \longrightarrow$$

$$Cd + 3261\overset{o}{A} + C_3H_8 + H_2 \longrightarrow$$
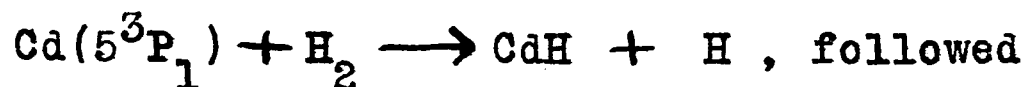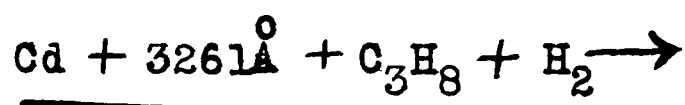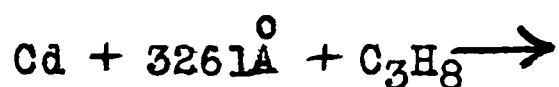
These reactions have been thoroughly investigated by Steacie, LeRoy and Potvin(81) at a temperature of 310° C. The quantum efficiency was found to be roughly 0.6 for both reactions.

For both reactions, the main products are hydrogen, and hexanes, together with smaller amounts of methane, butane, pentanes and heptanes.

There is no question that the C-H bond strength is greater than the excitation energy of $Cd(5^3P_1)$, viz. 87 kcal. Hence the primary process in the C_3H_8 reaction must be

$$Cd(5^3P_1) + C_3H_8 \longrightarrow CdH + C_3H_7 \text{ , followed}$$

by $CdH \longrightarrow Cd(5^1S_0) + H$.
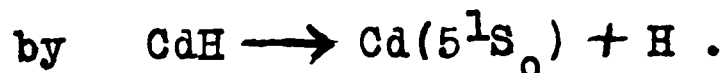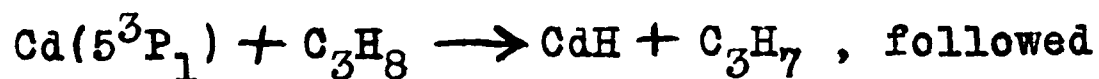
This gives us as the upper limit for the C-H bond strength in propane a value of $87 + 15.6 = 102.6$ kcal.

Now for the reaction of $C_3H_8 + H_2$ we must have in addition to the above

$$Cd(5^3P_1) + H_2 \longrightarrow CdH + H \text{ , then}$$
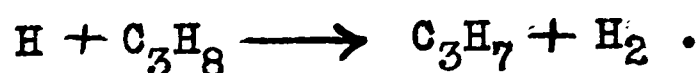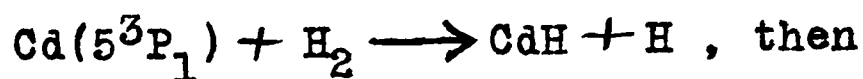
$$H + C_3H_8 \longrightarrow C_3H_7 + H_2 \text{ .}$$

And since rates of consumption of propane, and products of both reactions, are the same-practically, than both reactions must correspond to the same overall result, viz.

$$2C_3H_8 + Cd(5^3P_1) \longrightarrow 2C_3H_7 + H_2 + Cd(5^1S_0) \ .$$

On comparison with the mercury sensitized reaction of propane we see that the reactions are essentially the same.

The secondary reactions must be mainly

$$H + C_3H_8 \longrightarrow C_3H_7 + H_2 \ ,$$
$$2C_3H_7 \longrightarrow C_6H_{14} \ , \quad \text{plus some}$$
$$H + C_3H_7 \longrightarrow C_2H_5 + CH_3 \quad \text{(atom cracking step)},$$
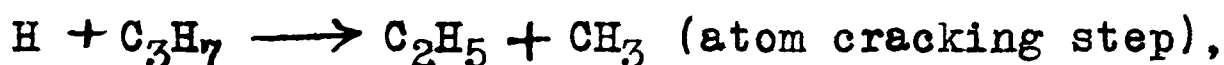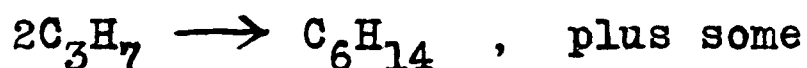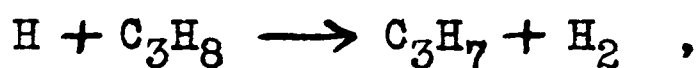
with a certain amount of radical decomposition and other minor reactions.

$$\underline{Cd + 3261\overset{o}{A} + C_2H_4 \longrightarrow}$$
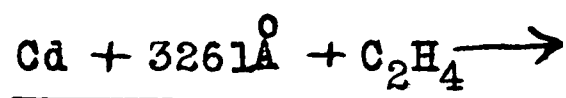
This reaction has been investigated by Steacie and Potvin(82,83) practically no reaction occured. What little polymerization that took place was ascribed to a quantum yield of the order of 0.01.

$$\underline{Cd + 3261\overset{o}{A} + C_2H_4 + H_2 \longrightarrow}$$
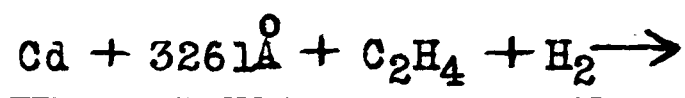
This reaction was the first cadmium photosensitization to be studied and was investigated by Taylor and Bates(53), who reported no hydrogenation to ethane, but that some polymerization of the ethylene took place.

The reaction was quantitatively investigated by Steacie and Potvin(82,83) at a temperature of 280°C.,who obtained a quantum yield of about 0.6 for the reaction. The products of the reaction are methane, ethane, propane, butane, propylene and higher hydrocarbons; butane being formed in the greatest quantities. This indicates that the reaction is very similar to the mercury sensitized reaction.

The primary is undoubtadly

$$Cd(5^3P_1) + H_2 \longrightarrow CdH + H \text{ , followed}$$

by

$$H + C_2H_4 \longrightarrow C_2H_5 \text{ ,}$$

$$2C_2H_5 \longrightarrow C_4H_{10} \text{ , and due to high}$$

temperatures also $H + C_2H_5 \longrightarrow 2CH_3$, plus a small amount of other various radical decompositions.

$$\underline{Cd + 2288\overset{o}{A} + C_2H_4 \longrightarrow}$$
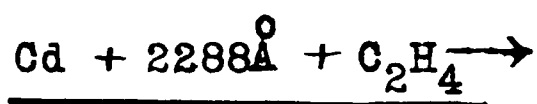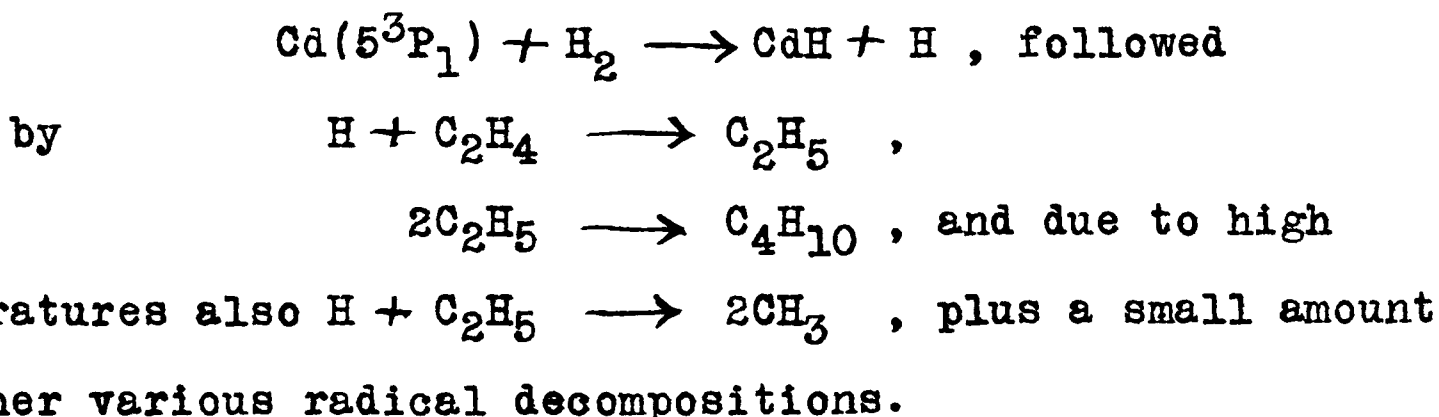
Is under investigation by Steacie and LeRoy(84). The initial pressure rise as found with the $Hg(6^3P_1)$ case has not been found for this reaction; and very little C_2H_2 is formed here. Liquid products of the polymerization appear to be mainly olefines of C_4 to C_6 range.

It is likely that the following mercury sensitization does not go, $Hg(6^3P_1) + C_2H_4 \longrightarrow C_2H_3 + H + Hg(6^1S_0)$

$$or \longrightarrow C_2H_3 + HgH \text{ , because}$$

Of the large bond strength value of C-H in C_2H_4, i.e. energy restrictions.

But there is no doubt that there is sufficient energy for the reaction $Cd(^1P_1) + C_2H_4 \longrightarrow CdH + C_2H_3$, which may be the primary step. If this is so, we will undoubtedly have $\qquad H + C_2H_4 \longrightarrow C_2H_5$,very fast , and possibly $\qquad C_2H_3 + C_2H_4 \longrightarrow C_4H_7$, and then olefines could then arise thus

$$C_2H_5 + C_4H_7 \longrightarrow C_6H_{12} ,$$
$$C_4H_7 + C_2H_4 \longrightarrow C_4H_8 + C_2H_3 , \text{ etc.}$$
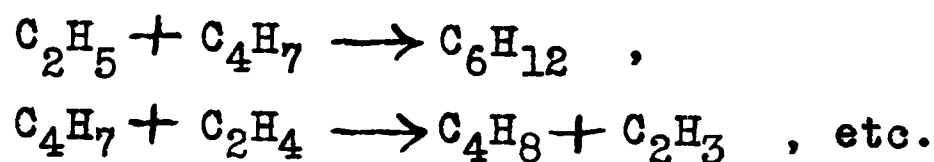
The mechanisms that have been suggested are in general the best of the many possible for the reactions that have been discussed. They have been chosen because they best represent the present data and state of knowledge on the subject. There is no doubt that with further research they will be revised and replaced with new ones.

ZINC PHOTOSENSITIZED REACTIONS OF ETHYLENE

EXPERIMENTAL

WE have seen that photosensitization opens up an interesting field of chemical research. It also was shown how bond strengths could be compared with energy presented by the sensitizer and by using all possible sensitizers and resulting reactions we can arrive at the value of a bond strength. Aside from bond strength, we find that we have entered into the field of radical and atomic reactions which has been the most interesting feature of photosensitization as yet.

So for obvious reasons which the reader will have realized in the perusal of this thesis, it was decided that the development of a suitable source of zinc resonance radiation for photosensitization and then its application would be a valuable contribution to physical-chemistry.

Accordingly this has been carried out by the author.

The experiments and results received now follow under the following headings:

1, The zinc resonance lamp.

2, Spectrograms.

3, Static pressure runs.

4, Runs for the production and test for acetylene.

5, Runs in a circulating system.

THE ZINC RESONANCE LAMP

Bender[21] developed a source of zinc radiation together with that of hydrogen and zinc hydride. This attempt was the closest till now in the development of the zinc resonance lamp that finally evolved out of this work.

Following up the work of Steacie and Potvin[82], attempts were made to construct both a plain and combined unit. The plain lamp consisted of 20 cm. of 0.6 corex-D tubing at the ends of which were sealed standard electrodes used in neon signs. The lamp contained a pellet of zinc and 3 mm. of neon, the filling was by the standard technique used in neon sign practice.

The combined unit was essentially the same, but the reaction vessel was sealed on to the discharge tube and the tube was in the form of a spiral.

The use of corex-D was for the purpose of filtering out the lower zinc resonance line 2139$\overset{o}{A}$. Initial success soon turned to failure as it was found that the corex-D could not stand up to the discharge at temperatures of $330^{o}C.-400^{o}C.$ the working range of the zinc lamp. The corex-D was apparently penetrated by the zinc or activated zinc. And in that portion of the tube

where the current density, i.e. the temperature, was highest a yellow colored discharge was emitted, as compared to the brilliant white-blue usually seen from the visible part of the zinc spectrum, this is probably due to sodium being liberated from the attacked glass. Incidentally when the lamp's emission is of a mauve color the $3075\overset{o}{A}$ resonance line is partly or completely absent.

Success was finally achieved by using a quartz tube of 15 cm. length and of 1 cm. diameter to which the pyrex electrode chambers were attached by means of graded seals.

The pyrex electrode chambers were 2.5 cm. in diameter and 10 cm. long. The electrodes were standard neon sign "coated" electrodes 1.2 cm. in diameter and 4 cm. long, while the hollow ends of the electrodes were crimped around porcelain rings. The electrodes were joined through nickel to tungsten wires which were sealed through the glass. A short side tube or projection contained a pellet of crystal zinc metal, and 3 mm. of neon was used as the carrier. The bombardment of the electrodes, filling, etc. were done by the Claude Neon Eastern Ltd. The resonance lamp is shown in figure II .

The lamp was connected to an ordinary neon sign transformer of 6000 volts, it ran at a voltage of about 500 and the current was 110 milli-amps.

Figure II

The zinc resonance lamp .

The following set of readings shows the relative intensity variation brought about by means of a variable resistance in series with the transformer primary and observed through a red-purple corex-A filter No. 986 Corning by a photronic cell in connection with a galvanometer.

Table V

Current through lamp , m.a.	Relative intensity galv- scale, cm.
110	3.8
82	3.5
66	3.2
40	2.4

It soon became apparent that the electrodes were not built for temperatures of $350-400°C$. for the lamp lasted only from 5 to 120 hours before burning out.

The weak spot was the tungsten through pyrex seal which at a temperature of $350°C$. or more either slowly leaked or cracked due to differences in the coefficients of expansion at this temperature.

The electrodes deteriorated due to sputtering which was generally quite considerable; a few lamps due to possible variations in the filling process did not sputter as much as others. Some of the sputtering was carried down the tube and deposited on the walls of the lamp in a

brown film which would decrease the light intensity. The amount and rate of film deposit depending on the temperature at which the lamp was used and on the individual lamp itself.

Added to this was the occa-sional graded seal that did not leave the bombarding without strain and consequently cracked on heating up for use. The occaisional electrode would drop off from the nickel mounting a result probably of much bombarding of the electrode which was necessary so as to completely de-gasify the insides of the lamp; more so in the case of a zinc lamp since it is to be used at such high temperatures.

The lamp was placed in an electric furnace of 20 cm. inside diameter; a size such that it could also contain the reaction vessel and minor accessories of the lamp such as heating and cooling coils placed around the electrode chambers, see figure IV.

The cooling coils consisted of spirals of annealed copper tubing 1/16th in. inside bore through which cool air could be passed when desired.

The heating coils consisted of helixes of small size nichrome wire on a drum of asbestos paper. By use of the cooling and heating coils it was possible to control the zinc vapor in the lamp making it distil back and forth or keeping one electrode cold enough so that the zinc did not condense out on the emitting part of the tube , natural temperature gradient of the furnace at times was sufficient for this.

This lamp does not measure up to the more ideal Cario Lochte-Holtgreven lamp(87) modified by Ladenburg and Zehden(88) where instead of circulating the metal emitter the carrier(inert gas) is circulated and the metal vapor can never diffuse up the current of inert gas to come into contact with the exit window. But for the purposes of photosensitization this type of lamp can not be used satisfactorily.

The zinc resonance lamp, once equilibrium was established, worked satisfactorily within the temperature range of 340-380°C. and even up to 425°C. but at this temperature the lamp was not kept long due to fear of to rapid deterioration.

There is no doubt that with a large and carefully constructed furnace with controlled temperature gradient, especially at the ends where the electrodes of the lamp are, the lamp's working range could brought down to 320°C. and extended up to 450°C. or more; but the temperature gradient at the ends of the furnace will have to be such that the electrodes remain around 330°C. while the center of the furnace is at 450°C.

Table VI

Temperature °C.	Vapor pressure of zinc, mm.
275	0.0005
312	0.004
327	0.006
341	0.01
380	0.04

For the purposes of this investigation the lamp was run at a temperature range of from 345 to 375°C. which was well above the necessary temperature required for a sufficient vapor pressure of zinc of about 0.005 mm.

By observation with a photronic cell through a red purple corex-A filter which transmitts the $3075\overset{o}{A}$ resonance line and adjacent ultra-violet the fluctuations of the lamp's intensity once equilibrium had been established for an hour period was found to be 1 to 2%, for a four hour period 3 to 5%, and due to the lamp's fairly rapid deterioration in most cases this variation in part would be a slow drift towards less intensity.

Now from the point of view of short pressure runs or spectrograms made within an hours time the fluctuation is not so serious because a fluctuation of 3 to 5% is within the experimental error of the runs or spectrographic plate. But this variation in the long circulating runs made it quite impossible to get quantitative data for analysis; in one instance two lamps were used in one run.

No suitable method has yet presented itself for the calibration of the zinc lamp at 350°C. Two runs made on the photolysis of acetone indicated that one lamp had an intensity of the order of 10^{-6} einsteins per sec. Relative intensities of the two resonance lines cannot be accurately measured but spectrogram II indicates that the $3076\overset{o}{A}$ line is about 5 (to 2) times as intense as the $2139\overset{o}{A}$ line.

Different lamps had different intensities, the variation being such that a good lamp may have had 5 times the intensity of a poor one.

Note: During a run in the photosensitization of ethylene the formation of a polymer, $(CH_2)_n$, or a film of free carbon on the walls of the vessel contributed as much to the decline of observed intensity as did the lamp's deterioration itself.

SPECTROGRAMS

The spectrograms were taken by means of a small Hilger quartz spectrograph which was placed next to the furnace containing the annular quartz reaction vessel through which ran the zinc lamp;direct observation of it was made by means of a quartz window in the side of the furnace.

Thus with the spectrograph slit adjusted at the quartz window of the furnace, the light traveled directly from the lamp through the corex-D filter,if one was present, through the reaction vessel of width 2 cm.,through the quartz window and onto the slit of the spectrograph, as shown in figure III.

The slit of the spectrograph was anywhere from 30 to 100 cm. from the lamp,depending upon the intensity of light desired.

Exposures used varied from 1/2 to 64 secs.

Plates used were plain Eastman 40's and ultra-violet sensitized 40's 3 1/4 by 4 1/4 . The spectrograms showing the lower resonance line 2139$\overset{o}{A}$ are the ultra-violet sensitized plates.
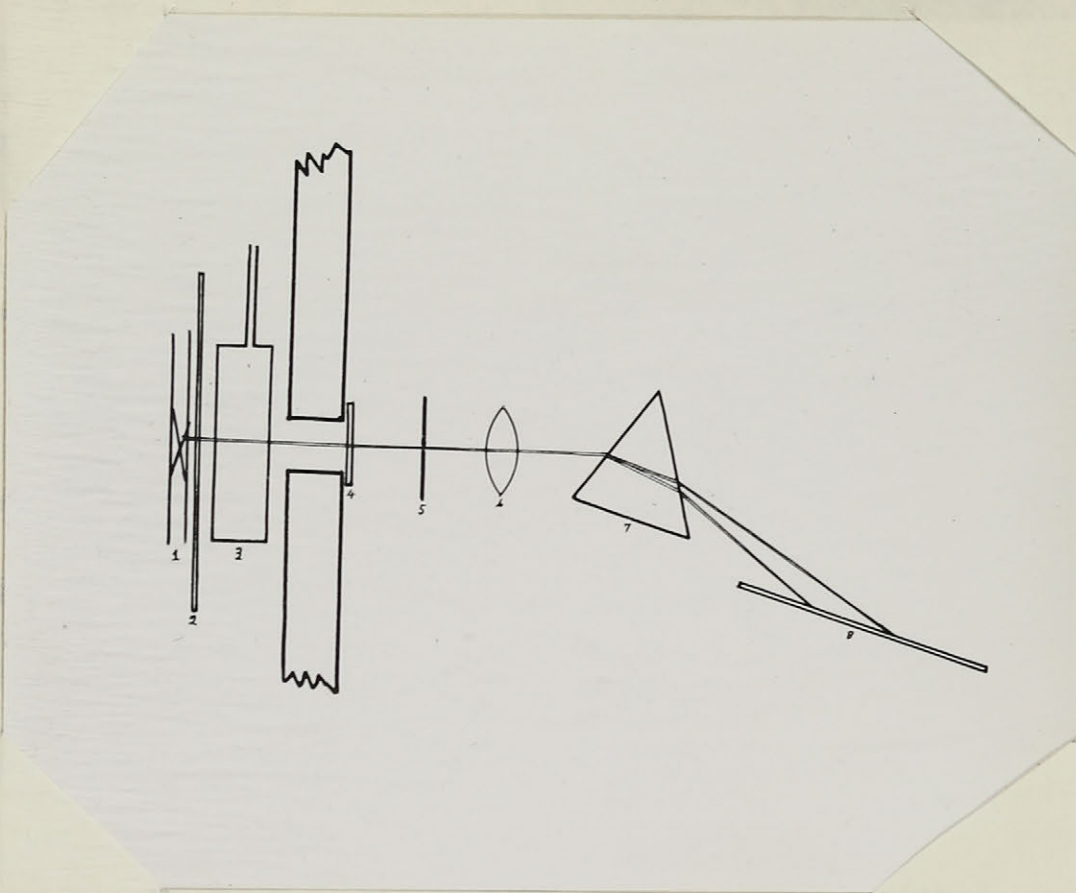
Figure III

1, Zinc lamp.

2, Corex-D filter.

3, Reaction vessel or cell.

4, Quartz window.

5, Spectrograph slit.

6, "   lense.

7, "   prism.

8, Spectrographic plate.

The absorption or'quenching'spectrograms were taken thus; the furnaces having been brought to the desired temperature, the foreign gas,ethylene, was slowly let into the reaction cell so as to pick up zinc vapor from the saturator, and an hour's time was allowed for complete mixing of the vapors. Then the lamp was turned on and after four minutes the desired exposures were taken, now some gas could be pumped away and still more exposures taken. Finally complete evacuation and exposures with the vessel empty of the foreign gas could then be taken.

Before developing,the sensitized plates were washed in ethylene-chloride for one minute so as to dissolve off the sensitizer(possibly the ethyl carboxylic ester of di-hydrocollidine), then the plates were dried by waving in the air.

The plates were developed in a suitable hydro-quinone developer for about 15 to 20 secs., fixed for 20 minutes and washed for an hour.

Spectrogram I is a sensitized 40 which is over exposed in order to show the complete zinc spectrum.

Spectrogram II is a sensitized 40 of the zinc spectrum in which different times of exposures are made starting with 1/2 sec. and ending at 16 secs.

Now by comparing the exposure times required to produce the same amount of blackening on the plate by the 3076$\overset{o}{A}$ resonance line and the 2139$\overset{o}{A}$ resonance line,

we see on the spectrogram plate or print that the 1 sec.
exposure of the 3076$\overset{o}{A}$ line is equivalent to or a little
greater than the 8 sec. exposure of the 2139$\overset{o}{A}$ resonance
line. Then with the approximate reciprocity law in mind
we can say that the intensity of the upper resonance line
is about 10 times as great as that of the lower.
But in spite of sensitization the sensitivity of the plate
will have fallen off by a factor of at least one half.
Then the intensity of the 3076$\overset{o}{A}$ resonance line is of the
order of 2 to 5 times that of the 2139$\overset{o}{A}$ resonance line.

Spectrogram III shows the efficiency of the
corex-D in filtering out the lower resonance line 2139$\overset{o}{A}$.

Spectrogram IV shows the effect of absorbtion
or 'quenching' of the 2139$\overset{o}{A}$ line (i.e. radiation) by C_2H_4, the
exposures having been varied for concurrent pairs.

Spectrogram V shows the effect of absorption of
the lower resonance line by C_2H_4, the exposures being the
same but concurrent pairs contain a variation in the press-
ure of C_2H_4 used.

Spectrogram VI is an attempt to show absorption
of the upper resonance line 3076$\overset{o}{A}$ by C_2H_4, a 40 cm. pressure
of ethylene being used in every other exposure. This
spectrogram as well as several others failed to detect
any absorption of the upper resonance line.

Most likely if a slight absorption of 10% existed, as relative polymerization rates seem to indicate, it would not be detectable by this method of direct observation.

Note: The corex-D filters were placed on the lamp so as to eliminate any possible interference from the 2139$\overset{o}{A}$ line.

From various plates showing the absorption of 2139$\overset{o}{A}$ by C_2H_4 it can be said that the 2139$\overset{o}{A}$ is absorbed 80% by 20 cm. of C_2H_4 and 40% by 10 cm.

This also seems to be the case with cadmium and C_2H_4; 15 cm. of C_2H_4 causing 80% absorption of the 2288$\overset{o}{A}$ cadmium resonance line while only about 15% of the 3261$\overset{o}{A}$ cadmium resonance line is absorbed.

A plate was made to see if any photochemical absorption of the 2139$\overset{o}{A}$ line by C_2H_4 could be detected; nothing was detected.
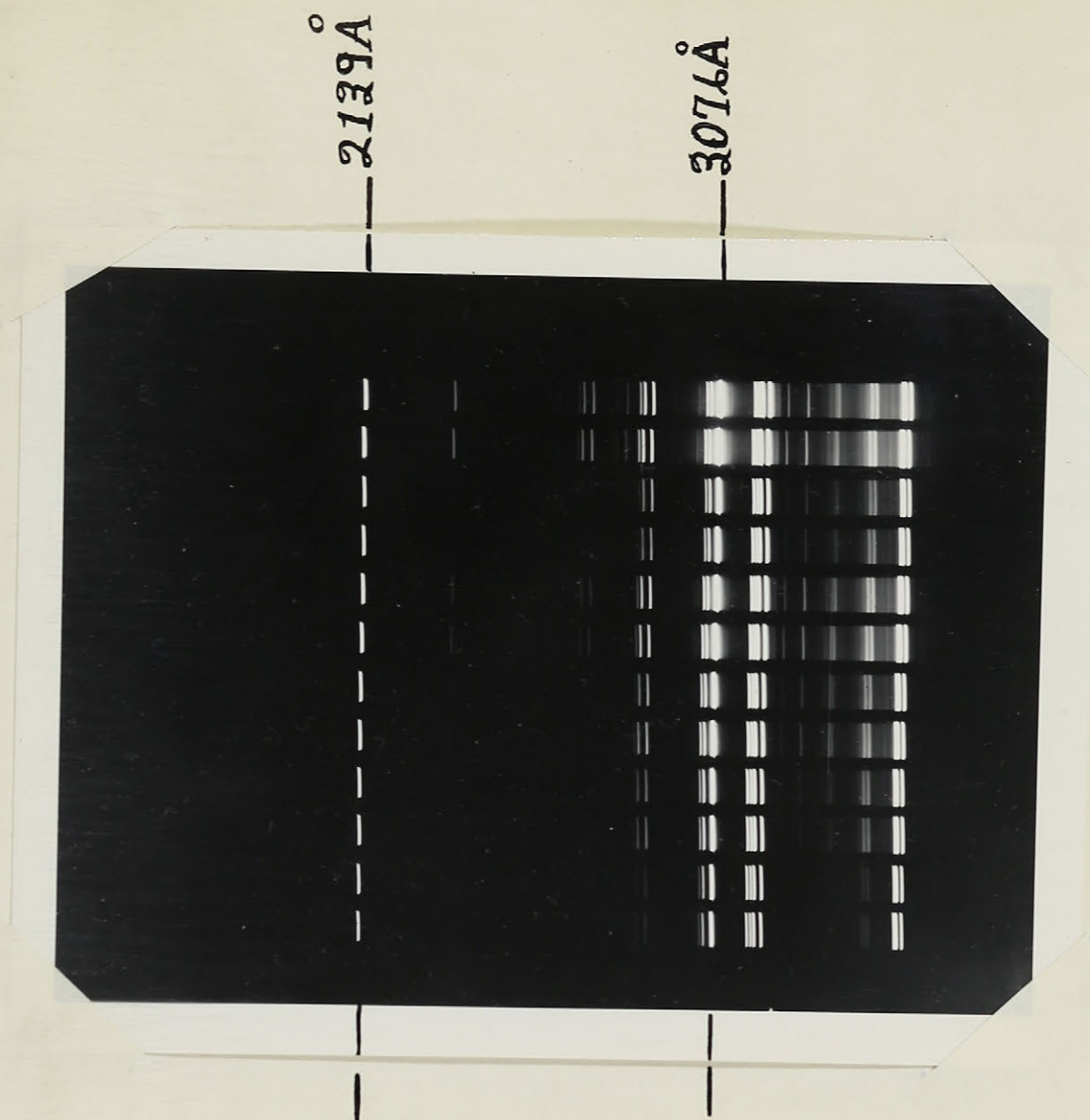
Spectrogram I

Exposure #	Exposuer time, secs.	Conditions: Temperature 355 C.
1	64	only zinc vapor in cell
2	64	"
3	16	"
4	16	"
5	32	"
6	32	"
7	16	"
8	16	"
9	8	"
10	8	"
11	4	"
12	4	"
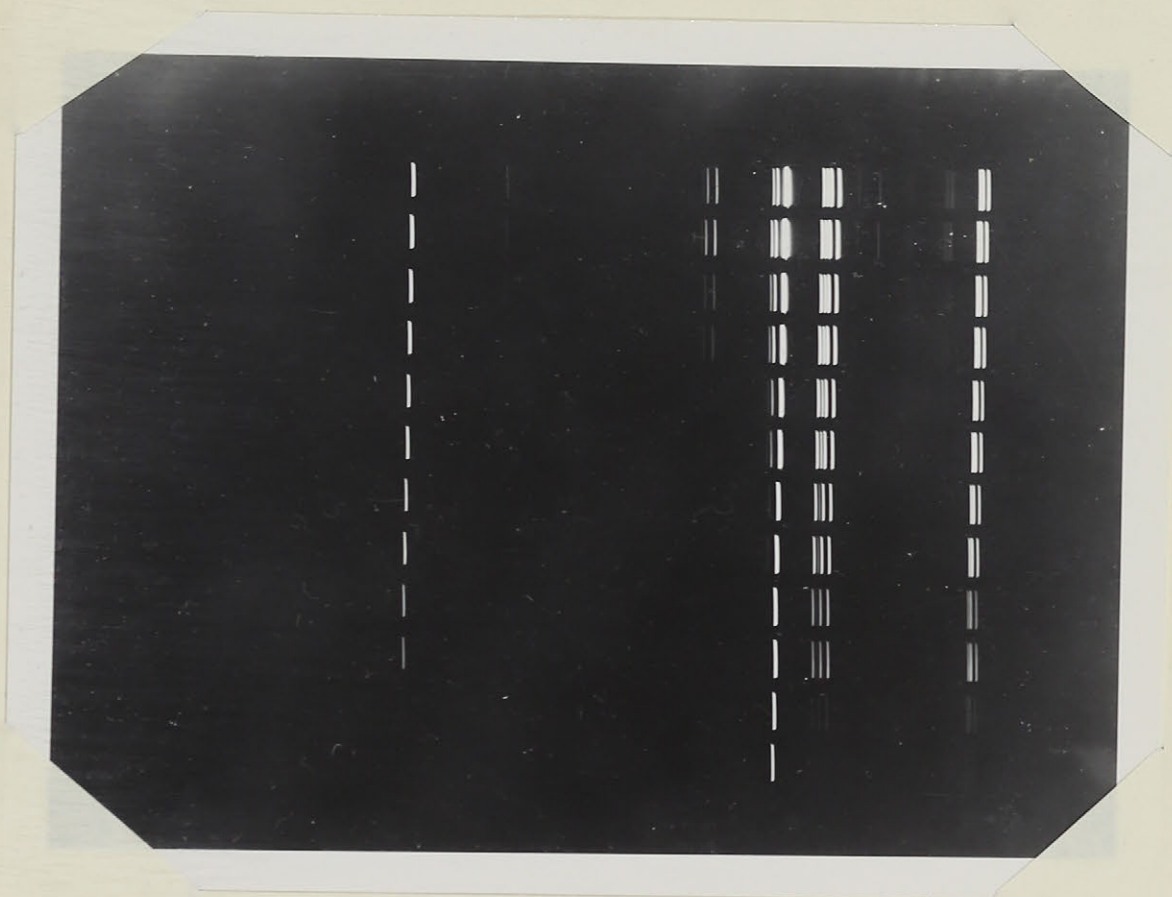
Spectrogram II

Exposure #	Exposure time, secs.	Conditions: Temperature 355°C.
1	16	only zinc vapor in cell
2	16	"
3	8	"
4	8	"
5	4	
6	4	etc.
7	2	
8	2	
9	1	
10	1	
11	3/4	
12	1/2	
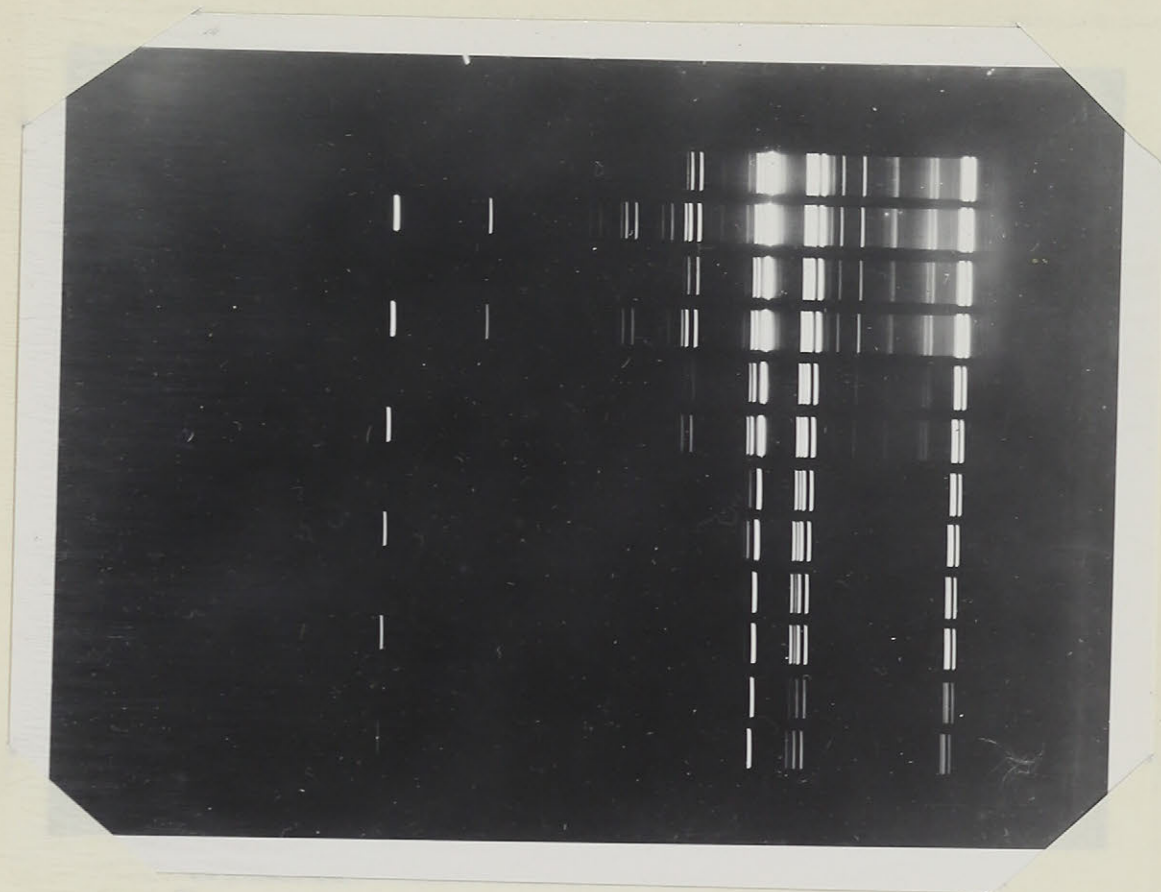
Spectrogram III

Exposure #	Exposure time, secs.	Conditions: Temperature 355°C.
1	64	Through corex-D
2	64	without corex-D
3	32	through corex-D
4	32	without corex-D
5	8	
6	8	
7	2	etc.
8	2	
9	1	
10	1	
11	1/2	
12	1/2	
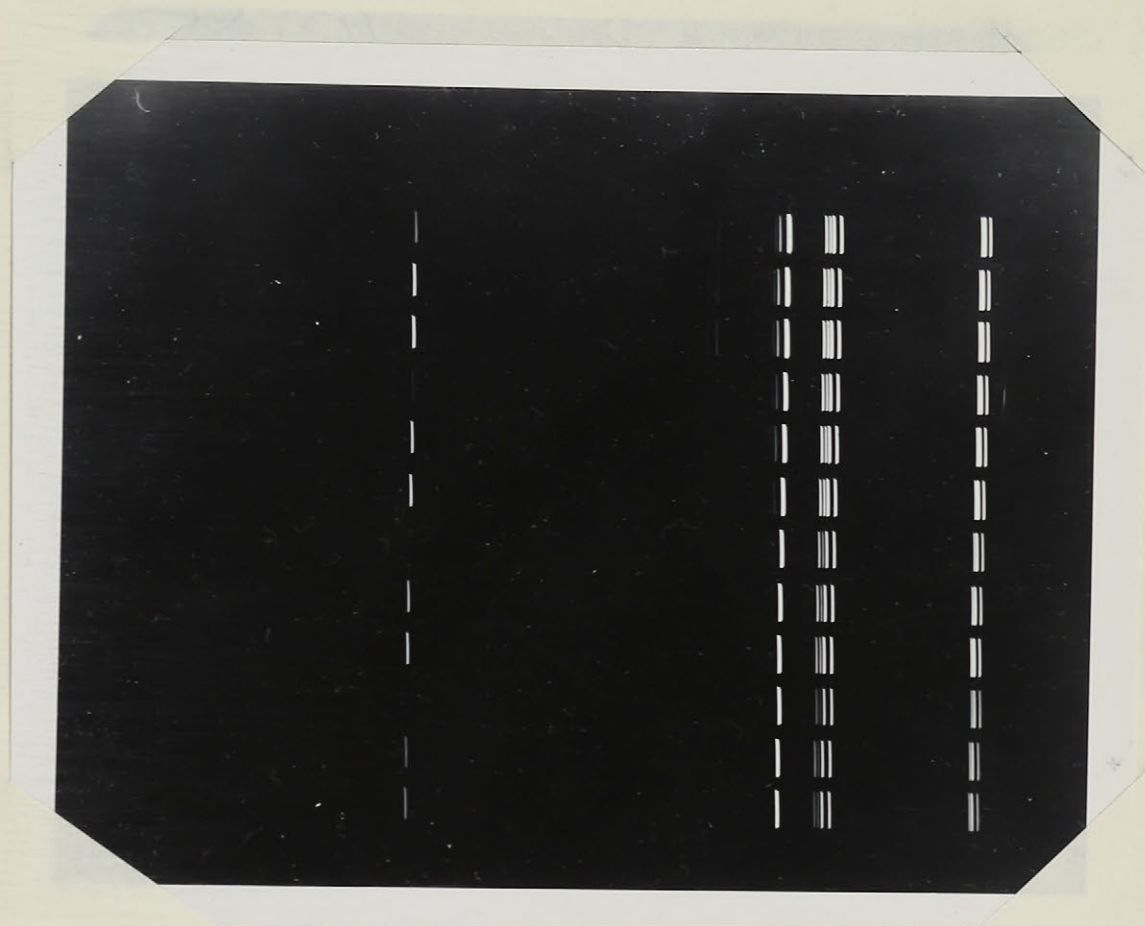
Spectrogram IV

Exposure #	Exposure time, secs.	Conditions: Temperature 355° C. Cell contains:
1	8	Zn vapor +C_2H_4(20 cm.)
2	8	Zn vapor(i.e. sat.hot)
3	8	O (i.e.satur.cold)
4	4	Zn vapor +C_2H_4(20 cm.)
5	4	Zn vapor(i.e. sat.hot)
6	4	O (i.e.saturator cold)
7	2	Zn vapor +C_2H_4(20 cm.)
8	2	
9	2	etc.
10	1	
11	1	etc.
12	1	
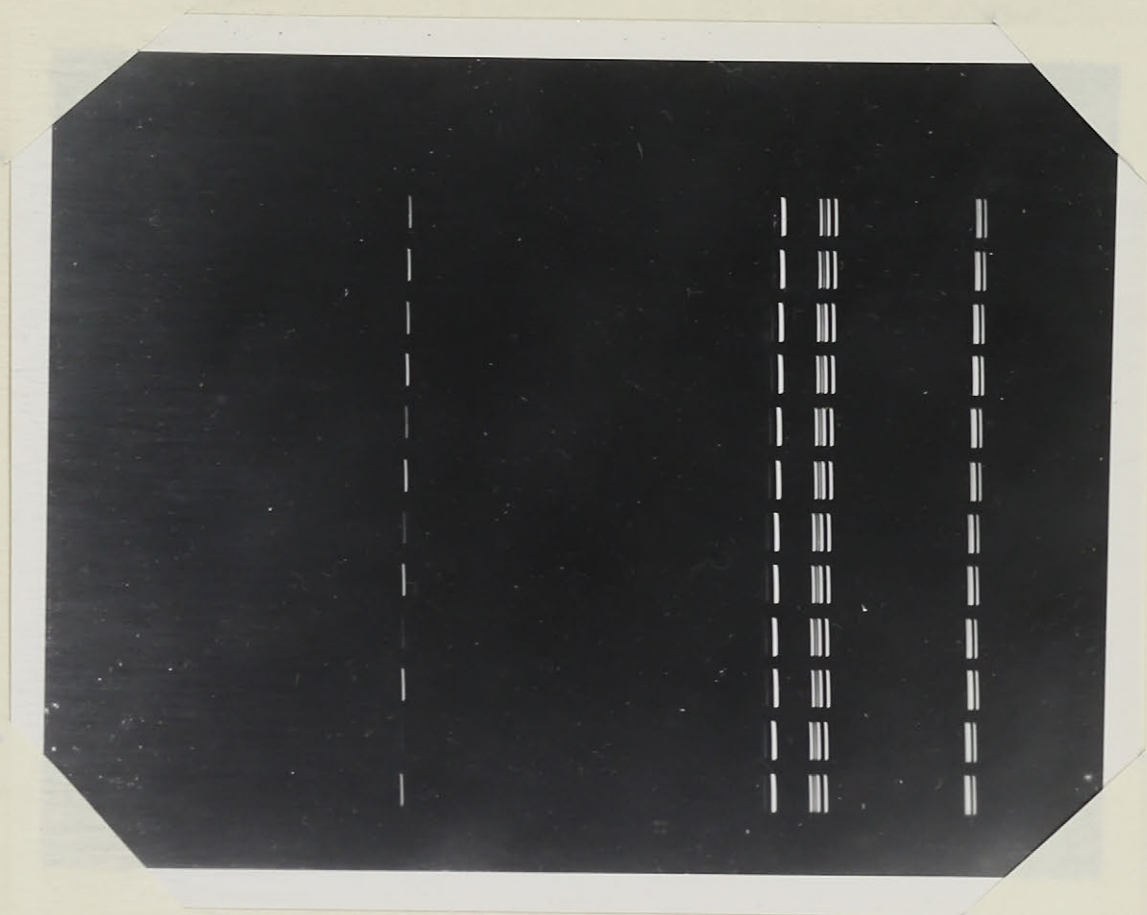
Spectrogram V

Exposure #	Exposure time, secs.	Conditions: Temperature $360°C.$ Cell contains:
1	3	Zn vap. + C_2H_4 (0.6 cm.)
2	3	Zn vap.
3	3	Zn vap. + C_2H_4 (2.0 cm.)
4	3	Zn vap.
5	3	Zn vap. + C_2H_4 (4.9 cm.)
6		Zn vap.
7		Zn vap. + C_2H_4 (9.9 cm.)
8	etc.	Zn.vap.
9		Zn vap. + C_2H_4 (19.4 cm.)
10		Zn vap.
11		Zn vap. + C_2H_4 (39.0 cm.)
12		Zn vap.
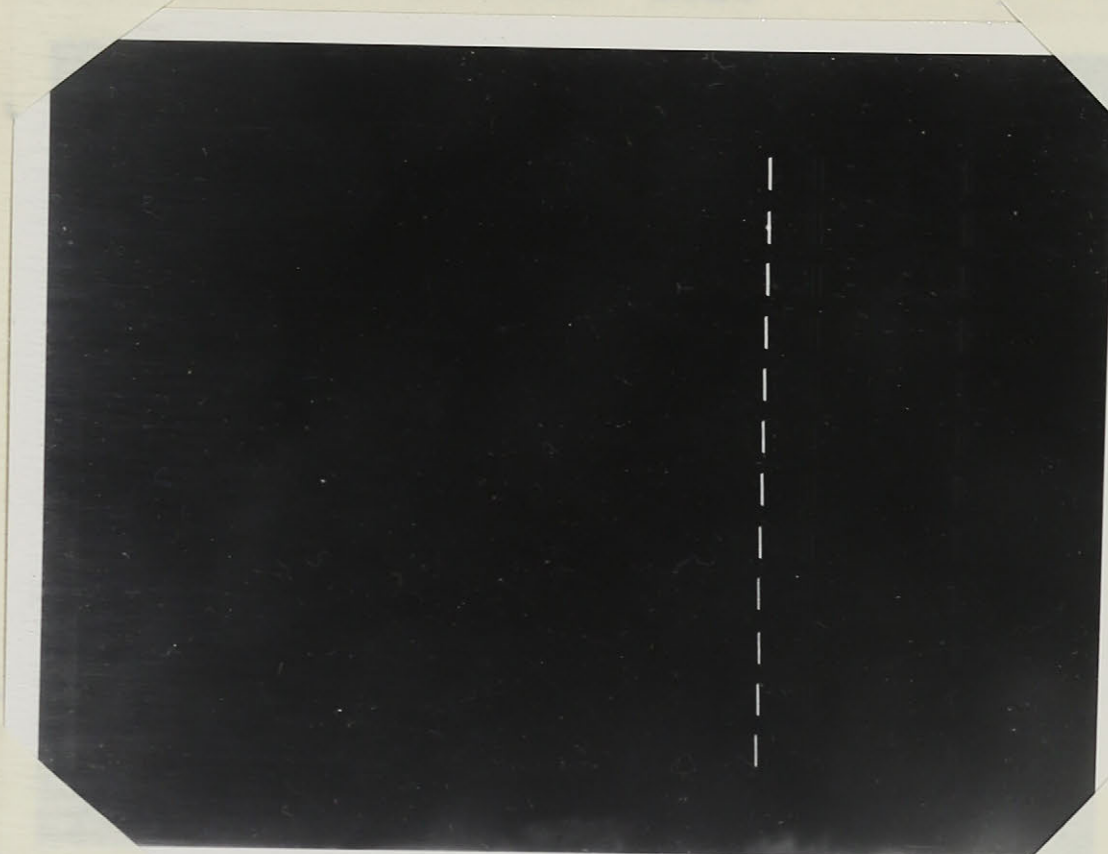
Spectrogram VI

Exposure #	Exposure time, secs.	Conditions: Temperature 360°C. Cell contains:
1	4	Zn vapor
2	4	Zn vap. $+ C_2H_4$ (40 cm.)
3	4	Zn vapor
4	4	Zn vap. $+ C_2H_4$ (40 cm.)
5	3	
6	3	etc.
7	3	
8	3	
9	2	
10	2	etc.
11	2	
12	2	

STATIC PRESSURE RUNS

The main features of the apparatus used in the pressure runs and throughout this work are shown in figure IV. There we find two furnaces electrically wound and well lagged with magnesia and asbestos paper. The large furnace contains the annular shaped fused quartz reaction vessel of length 10 cm., external diameter 8 cm. and internal diameter 4 cm.; and the lamp with its accessories and possibly the corex-D filter which consists of two halves of a lengthwise slit piece of 20 cm. long, 2 cm. diameter corex-D tubing.

The small furnace which is placed flush with one end of the large furnace contains the saturator an S formed combination of large and small glass tubing. The two large sections of this saturator contain a zinc tin alloy, a 1:1 mixture, of low melting point a precaution against a possible cracking of the pyrex tubing. The surface of alloy in the saturator is of the order of 50 sq. cm.

Incidently the quartz reaction vessel is united to the saturator, which is made of pyrex, by a graded seal;
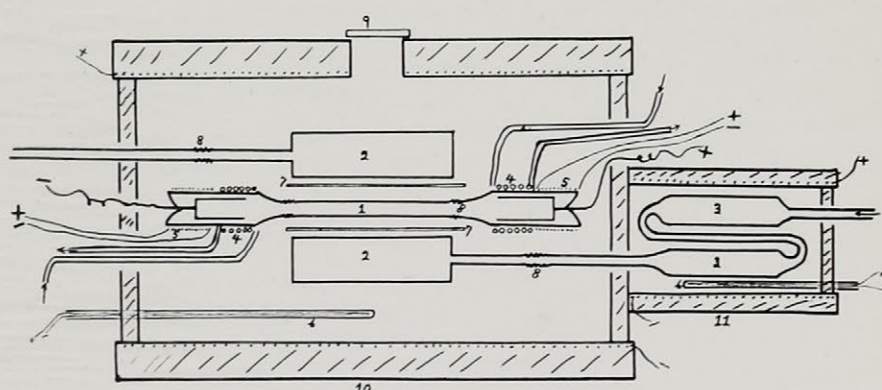
Figure IV

1, Lamp.
2, Quartz reaction vessel.
3, Saturator.
4, Copper cooling coil.
5, Heating coil.
6, Thermocouple.
7, Corex-D filter.
8, Graded seal.
9, Quartz window.
10, Furnace.
11, Furnace.

the opposite end also has a quartz to pyrex graded seal; this end can be stopped by a stopcock or opened for circulatory purposes. The line coming from the saturator leads to a three way stopcock and can be turned on to the circulating system or just opened to the vacuum line.

The vacuum line leads to the usual storage volumes, distillation traps, inlets to the system and the terminating trap, mercury pump and backing Cenco rotary pump.

Both the line coming from the saturator and the line coming from the opposite end of the furnace are as well connected to soft glass by De Khotinsky joints, since the remaining parts of the apparatus are built of soft glass.

The volume of the quartz cell is 340 cc. but the total volume of lines, manometer, saturator and vessel itself in the static system is 610 cc. at room temperature. The manometer used in the runs is the ordinary vacuum bulb U shaped type.

Ethylene was obtained in small cylinders from the Ohio Chemical and Manufacturing Co. The purity was such that five fractionations using liquid air as condensing agent gave ethylene in which no impurities could be detected with the methods of analysis used.

The hydrogen came from commercial cylinders and was purified by passing over platinized asbestos at 600°C. and then through a liquid air trap.

The furnaces were hand regulated to a temperature variation of less than $\pm 1^{o}$C., because no other convenient method of thermostating to such accuracy at 350°C. was at hand.

During the first runs made the saturator was kept at a temperature that was 5°C. higher than the main furnace but this was soon found to be of no added advantage and in latter runs the temperature of the saturator was kept the same as that of the main furnace.

The temperatures in the furnaces were measured by means of chromel-alumel thermocouples together with a standard Cambridge potentiometer with the cold junctions of the thermocouples in oil baths at room temperature.

With furnaces up to the required temperature and the system having been evacuated to 10^{-4} of a mm., a run was carried out in the following manner: The lamp is turned on and left going for several minutes untill it has come to equilibrium. Then 20 cm. of ethylene is smoothly let into the reaction vessel, passing first through the saturator where it picks up sufficient zinc vapor, then it goes into the reaction vessel. A first reading of the pressure is taken and a stop watch is set going. At first readings are taken every two or three minutes and towards the end of the run every 10 minutes or so. The average run being of about one hour duration. During this time the temperature is kept constant to within $\pm 1^{o}$C.

A sample run containing all details noted during the run follows:

A Static Run with Ethylene Alone, and without Corex-D filters.

Temperature of Furnace 360°C.

Temperature of Saturator 360°C.

Lamp Current 108 m.a.

Time, Min.	Pressure, cm.	Variation in Furnace temp., °C.	Variation in Saturator temp., °C.
0	20.73	0	+ 0.2
2	20.64	− 0.2	+0.3
4	20.56	+0.2	+0.3
8	20.42	+0.2	+0.3
15	20.19	− 0.3	+0.2
24	19.96	−0.2	+0.8
31	19.79	0	+0.2
43	19.55	− 0.2	+0.8
61	19.20	−0.2	+0.8

Note: This run is shown as curve II in figure V.

Runs made directly for the purpose of observing the pressure change and some made incidentally later on are included in the following tables.

Runs were made with ethylene alone and with 1:1 mixtures of ethylene and hydrogen; with no corex-D filter

ΔP in m.m.

I

II

Time in mins.
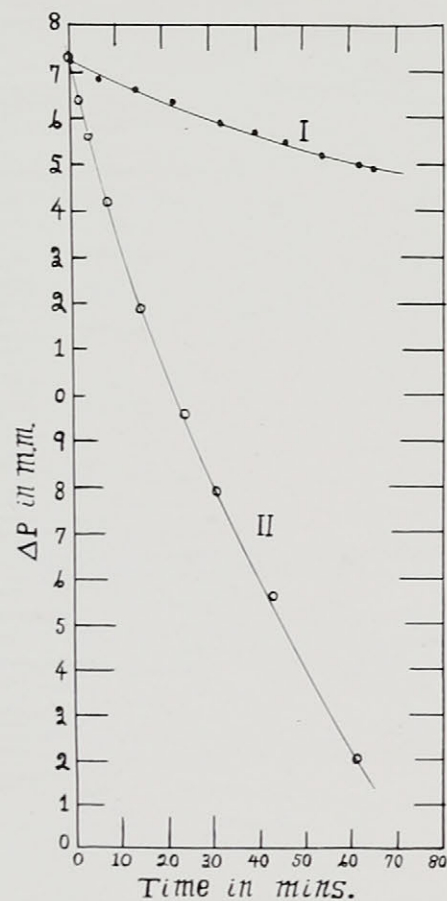
Figure V

Curve I, shows pressure change in C_2H_4
when exposed to the 3076Å resonance line.

Curve II, shows pressure change in C_2H_4
when exposed to the 2139Å and the 3076Å
resonance lines.

i.e. exposing the reactants to both the 3076Å and the 2139Å resonance lines, and with a corex-D filter, exposing the reactants to only the 3076Å resonance line.

For a typical set of pressure variation curves showing the polymerization rate of ethylene alone, with and without a corex-D filter, see figure V. The two runs depicted in figure V were made with the same lamp, one immediately after the other.

It should be noted that the slow deposit of $(CH_2)_n$ polymer or carbon in the reaction vessel necessitated an occaisional flaming of the vessel with a stream of oxygen flowing through it. In spite of this and lamp deterioration, rates were generally reproducible to the first figure which is all that can be asked for.

The following tables give conditions and rates obtained in the static pressure runs.

Static Runs with Ethylene Alone

Table VII

Lamp I , with corex-D filter. 20 cm. C_2H_4 .

Run #	Corex-D filter	Temperature, $^\circ$C.	Rate of poly-merization, mm./min.	Remarks
1	yes	355	0.07	
2	yes	355	0.0002	thermal blank run
3	"	362	0.08	
4	"	362	0.07	
5	"	362	0.07	
6	"	362	0.016	blank in which-only a little Zn vap.
7	"	362	0.013	" " " " " " " " "
8	"	355	0.08	
9	"	355	0.07	
10	"	355	0.07	
11	"	355	0.07	
12	"	365	0.065	
13	"	365	0.06	
14	"	375	0.08	
15	"	375	0.08	
16	"	365	0.063	

Here the average rate is ~0.07 mm./min. and there is

a negligible increase in rate with temperature increase

from 355°C. to 375°C.

Static Runs with Ethylene Alone

Table VIII

Lamp I, without corex-D filter. 20 cm.C_2H_4 .

Run #	Corex-D filter	Temperature, $^{\circ}C.$	Rate of poly- merization, mm./min.	Remarks
1	no	355	0.49	slow decline in rate due possibly to lamp intensity falling and especially to polymer or C deposit on vessel walls.
2	no	355	0.48	
3	no	355	0.42	
4	"	365	0.40	
5	"	365	0.42	
6	"	345	0.41	
7	"45	345	0.42	
8	"	375	0.38	
9	"	375	0.37	
10	"	375	0.46	a 35 cm. run corrected to 20 cm.
11	"	375	0.29	a 10 cm. run corrected to 20 cm.

Average rate is approximately 0.5 mm./min.

and there is no detectable variation in rate with temperature

increase from 345°C. to 375°C.

Static Runs with Ethylene and Hydrogen
Mixtures

Lamp I, without corex-D, 20 cm. of C_2H_4 and H_2 in 1:1 mixture or 40 cm. of same with rate corrected to 20 cm.

Table IX

Run #	Corex-D filter	Temperature, ^{0}C.	Rate of poly- merization, mm./min.	Remarks
1	no	355	1.4	
2	no	355	1.5	mixture: 29.8 cm, H_2 29.2 " C_2H_4
3	"	"	1.3	
a	"	"	0.29	ethylene alone, check run.
4	"	"	1.7	
b	"	"	0.3	ethylene alone check run.
5	"	"	1.9	
6	"	"	2.0	
c	"	"	0.34	ethylene alone check run.

The check runs of 'ethylene alone' show a marked decrease in rate as compared with table VIII runs, i.e. a decrease in the light intensity. Accordingly the average rate of polymerization of 1:1 mixtures of C_2H_4 and H_2 may for comparative purposes be corrected in proportion to the change in the rate of polymerization of the 'ethylene alone' runs. Thus the average rate of polymerization 1.7 by the above table may be corrected to 2.5 in accordance with the ratio of 0.5/0.3 .

Static Runs with Ethylene and Hydrogen

Mixtures and with 'Ethylene alone'

Table X

Lamp II , mixture ratio 1:1, etc.

Run #	Corex-D filter	Temperature, °C.	Rate of poly- merization, mm./min.	Remarks
0	yes	355	0.000	'C$_2$H$_4$ alone' thermal blank.
a	"	"	0.021	'C$_2$H$_4$ alone'
b	"	"	0.022	" "
1	"	"	0.61	C$_2$H$_4$ & H$_2$ mixt.
c	"	"	0.023	'C$_2$H$_4$ alone'
2	"	"	0.79	C$_2$H$_4$ & H$_2$ mixt.
d	"	"	0.022	'C$_2$H$_4$ alone'
3	"	"	0.64	mixt.
e	"	"	0.020	alone
4	"	"	0.55	mixt.
f	"	"	0.025	alone
5	"	"	0.79	mixt.

The average rate of polymerization of 1:1 mixture of C$_2$H$_4$ & H$_2$ with corex-D filter and with the new lamp is 0.7 mm./min. Whereas the rate of polymerization of 'C$_2$H$_4$ alone' with filter and new lamp is 0.022.

Static Runs with Ethylene and Hydrogen

Mixtures and with'Ethylene Alone'

Table XI

Lamp II , mixture ratio 1:1, etc.

Run #	Corex-D filter	Temperature, $^{\circ}C$.	Rate of poly- merization, mm./min.	Remarks
a	no	355	0.22	'C_2H_4 alone'
1	no	355	0.80	C_2H_4 & H_2 mixt.
b	"	"	0.23	alone
2	"	"	0.88	mixt.

The average rate of polymerization of 1:1 mixture

of C_2H_4 & H_2 without corex-D filter and by lamp II is

0.84 mm./min. While the rate of polymerization of ethylene

alone without corex-D filter and by lampII is 0.22 mm./min.

Later runs in conjunction with later work

give the following results in table XII and XIII:

Static Runs with Ethylene Alone

Table XII

Lamp VI , 20 cm. C_2H_4

Run #	Corex-D filter	Temperature, $^\circ$C.	Rate of poly- merization, mm./min.	Remarks
1	no	360	0.5	'ethylene alone'
2	no	"	0.5	" "
3	yes	"	0.05	" "
4	yes	"	0.05	" "
5	no	"	0.45	" "
6	no	"	0.5	" "

Table XIII

Lamp VII, etc.

1	no	360	1.07	'ethylene alone'
2	no	"	0.86	" "
3	yes	"	0.11	""
4	yes	"	0.11	""

Note: Vessel was Flamed before runs 1, 3 and 4 .

Tables XII and XIII indicate a rate ratio of

1:10 for rates of polymerization of'C_2H_4 alone'with and

without corex-D filter.

The selected results are summarised thus:

Lamp	Table	Rate of poly-merization, mm./min.	Reaction
I	VII	0.07	C_2H_4 $3076\overset{o}{A}$
	VIII	0.50	C_2H_4 $3076\overset{o}{A}$ $2139\overset{o}{A}$
	IX	2.8	C_2H_4 H_2 $3076\overset{o}{A}$ $2139\overset{o}{A}$
II	X	0.022	C_2H_4 $3076\overset{o}{A}$
		0.70	C_2H_4 H_2 $3076\overset{o}{A}$
	XI	0.22	C_2H_4 $3076\overset{o}{A}$ $2139\overset{o}{A}$
		0.84	C_2H_4 H_2 $3076\overset{o}{A}$ $2139\overset{o}{A}$
VI	XII	0.05	C_2H_4 $3076\overset{o}{A}$
		0.5	C_2H_4 $3076\overset{o}{A}$ $2139\overset{o}{A}$
VII	XIII	0.11	C_2H_4 $3076\overset{o}{A}$
		1.1	C_2H_4 $3076\overset{o}{A}$ $2139\overset{o}{A}$

Apparently lamps II, VI and VII, although possessing different intensities, give the same relative intensity between the two resonance lines. Accordingly from tables X to XIII it can be said that the polymerization rate of C_2H_4 by the zinc resonance lamp without the corex-D is 10 times greater than the rate with the corex-D. I.e. the rate induced by the $Zn(4^3P_1)$ state plus the $Zn(4^1P_1)$ state

is ten times that induced by the $Zn(4^3P_1)$ state alone.

From tables X and XI we can make the following table of relative rates and compare them with the corresponding relative/rate with cadmium.

Table XIV

Line $\overset{o}{A}$	Reaction	Relative rate	Corresponding relative rate with cadmium
3076	C_2H_4	0.031	0.04
3076&2139	C_2H_4	0.31	0.42
3076	$1C_2H_4 + 1H_2$	1.0	1.0
3076&2139	$1C_2H_4 + 1H_2$	1.2	1.3

With this table in mind a casual speculation can be made which indicates the order of magnitude of the effects in the above reactions.

By making the plausible assumption that the mixture $C_2H_4 + H_2$ quenches both resonance lines to the same extent and assuming that the reaction is the same whither the hydrogen absorbs the 3076$\overset{o}{A}$ or the ethylene absorbs the 2139$\overset{o}{A}$, than from the relative rates of 1 to 1.2 it can be said that this indicates an intensity for the 3076$\overset{o}{A}$ resonance line of five times that for the 2139$\overset{o}{A}$ resonance line.

Now assuming a quantum yield of 0.5 for the hydrogen, ethylene reaction, which is reasonable since the same reaction with cadmium has a quantum yield of about 0.5 to 0.7, and assuming that the pressure decrease is given essentially by the following equations in the respective cases

$$2C_2H_4 \longrightarrow C_4H_8 \quad \text{and} \quad 2C_2H_4 + 2H_2 \longrightarrow 2C_4H_{10} ,$$
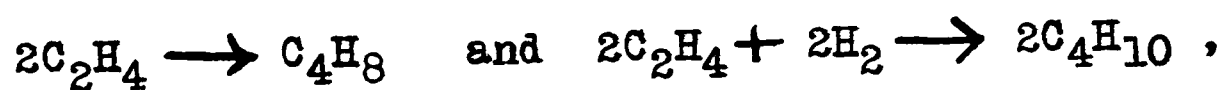
it can than be said that the quantum yield of the reaction $C_2H_4 + 3076\overset{o}{A} + 2139\overset{o}{A} \longrightarrow$, by comparing rates 0.31 and 1.2 with the quantum yield 0.5, is __0.13.__

Similarly the quantum yield for the reaction

$$C_2H_4 + 3076\overset{o}{A} \longrightarrow$$, by comparing 0.031 and 1.0

with 0.5, is found to be 0.016 .

RUNS FOR THE PRODUCTION OF, AND
TESTS FOR ACETYLENE

As in the analogous sensitized reaction with
mercury, acetylene was expected as a product in the present
investigation; but preliminary runs and tests did not
indicate the presence of any C_2H_2 . However with more
accurate analytical methods it was found that a small
amount of acetylene was produced in the zinc sensitized
reaction.

Accordingly runs were made in order to investigate
this production of acetylene. With the filter on, all
indications were that if there was production of C_2H_2
the rate was so slow and the consequent concentration
formed so small that it would not be detectable.
A final 20 hour, -125° C. trapping, circulatory run
with corex-D filters gave a little acetylene, 0.03%;
the amount seems to agree with what would be expected in
the comparison of rates with and without the filters.
But there is a possibility that this is due to a little
$2139\overset{o}{A}$ having been reflected out lengthwise along the
filters and having entered into the arms of the reaction
vessel.

In the production of C_2H_2 with the filters off there is enough C_2H_2 formed by static runs to be readily determined.

The following is an account of the analytical procedure used. An ordinary static run is made for a desired length of time . Then immediately all the gases, products and reactants, are condensed out into an evacuated 300 cc. spherical volume which is immersed in liquid air. Allowing five minutes for diffusion the stopcock on the spherical volume is then turned off and the vessel is detached from the outlet of the main apparatus.

The spherical volume,and attachments,stopcock and ground glass joints, necessary for the purposes desired, are shown in figure VI .

The residual pressure inthe main apparatus of the order of 0.5 mm. is noted; it is quite negligible and consists mainly of hydrogen.

The 20 cm. of C_2H_4 used in a run, and after reaction, gives about 100 cc. of gas at N.T.P.; consequently the sample of gas in the spherical vessel of 300 cc. capacity has a pressure well below atmospheric.

The next step is to insert the female end of the ground glass joint into a beaker containing a 2.5% solution of $AgNO_3$. The stopcock is then opened and 25 cc. of the solution is let in. The ends of the tube are rinsed with a little distilled water, the stopcock is turned off and the apparatus is then shaken well .
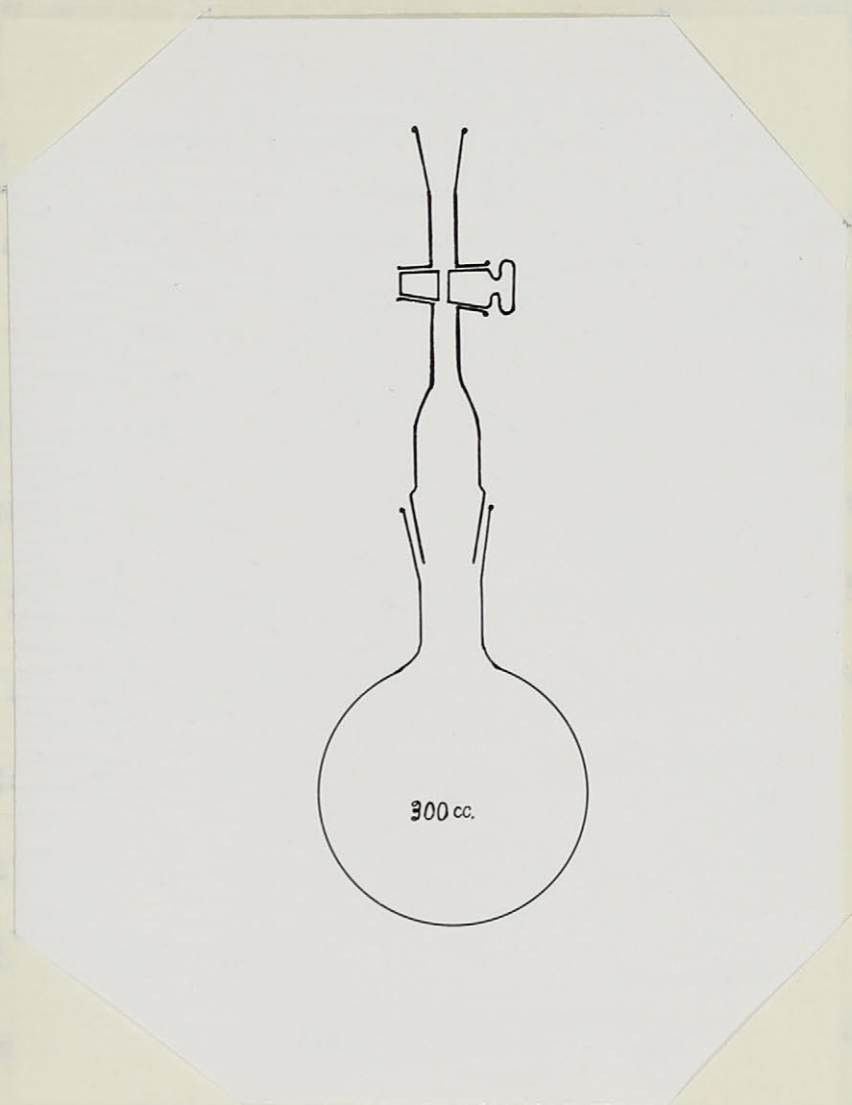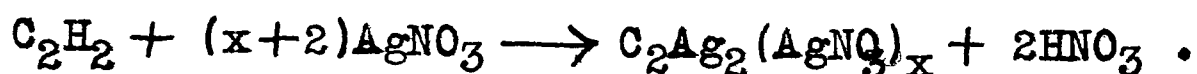
Figure VI

300 cc. analytical volume .

A white precipitate of $C_2Ag_2(AgNO_3)_x$ is formed by the reaction

$$C_2H_2 + (x+2)AgNO_3 \longrightarrow C_2Ag_2(AgNO_3)_x + 2HNO_3 .$$

The ground glass joint is now detached, i.e. at the large joint, and the detached part is rinsed into the spherical volume. Then 5 cc. of saturated NaCl solution is added in order to precipitate the excess Ag^+ . Finally a drop of brom cresol green, methyl red indicator is added and the solution is titrated with 0.01 normal NaOH .

Blanks on solutions, and blank runs were neutral with this indicator when fresh $AgNO_3$ was used.

This method of analysis is essentially that used by Ross and Trumbell(89).

The lamp and system were quite aged when these runs were made;hence the good consistancy in the rates of polymerization of these runs.

The data received from the runs are compiled in the following table. The percent production of acetylene with time of run is shown in figure VII , where it is seen that the acetylene production is rapidly approaching a maximum equilibrium concentration along the asymptote of 0.25% of acetylene.

Note: In circulatory run VIII,where the reaction vessel was newly cleaned and the reaction rate showed that the new lamp used was the most intense one used so far, about twice as intense as the one used in these acetylene runs, a concentration of 0.5% of C_2H_2 was obtained which
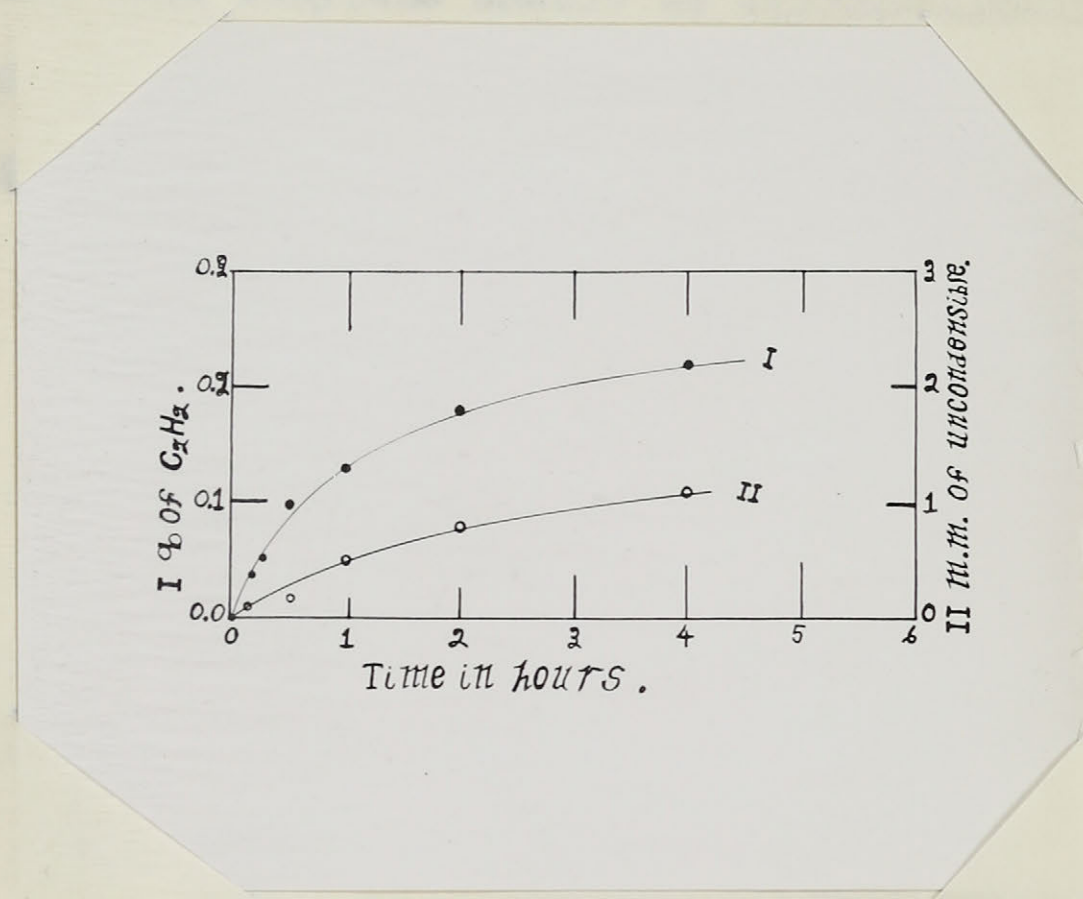
Figure VII

I, acetylene production curve.

II, uncondensible production curve.

after ten hours of reaction may be considered
to be the equilibrium concentration.

The pressure of uncondensible gases, mostly
hydrogen and some ethylene unable to diffuse, left in
condensing is also shown in figure VII, where it is evident
that the pressure of uncondensible is proportional to the
amount of C_2H_2 formed. *This* is to be expected since the
acetylene and hydrogen are formed by $C_2H_4 \longrightarrow C_2H_2 + H_2$.

Table XV

Temperature of runs:360°C.

Pressure of C_2H_4 used: 20 cm.

Volume of vessel: 340 cc.

Lamp VI . No corex-D filter.

Run #	Time, min.	%C_2H_2, mole	Uncondensible, mm.	Rate of poly-merization, mm./min.
1	60	0	0	0.002(thermal blank)
2	30	0.10	∿ 0.15	0.42
3	60	0.13	0.5	0.40
4	120	0.18	0.8	0.41
5	240	0.22	1.1	0.41
6	15	0.05	-	0.42
7	30	0.11	∿0.2	∿ 0.4
8	10	0.037	0.08(McL.gauge)	0.41

Note: Run 7 was made as a one point check, with run 2 ,
the analysis also was a check variation made according
to the Ross and Trumbell procedure.

RUNS IN A CIRCULATING SYSTEM

The effective volume of the static system was
not large enough to contain an amount of ethylene which
would give enough gaseous products for analysis.
Also another feature warranting a circulating system is
the oppertunity that it presents for the trapping out of
higher boiling products.

Accordingly the apparatus was built in such a
manner that when desired the system could be switched
from a static into a circulating one by the simple
procedure of turning two stopcocks.

The circulating part of the system is shown in
figure VIII. The essentials of the circulating part of the
system are a condensation trap, a mercury trap, a set of
mercury valves which keeps the gas flow going in one
direction in spite of the reciprocating motion of the pump.
The pump consists of a brass cylinder and an iron piston
which is moved by an electro-magnet which fits around the
brass cylinder. The electro-magnet is propelled by a
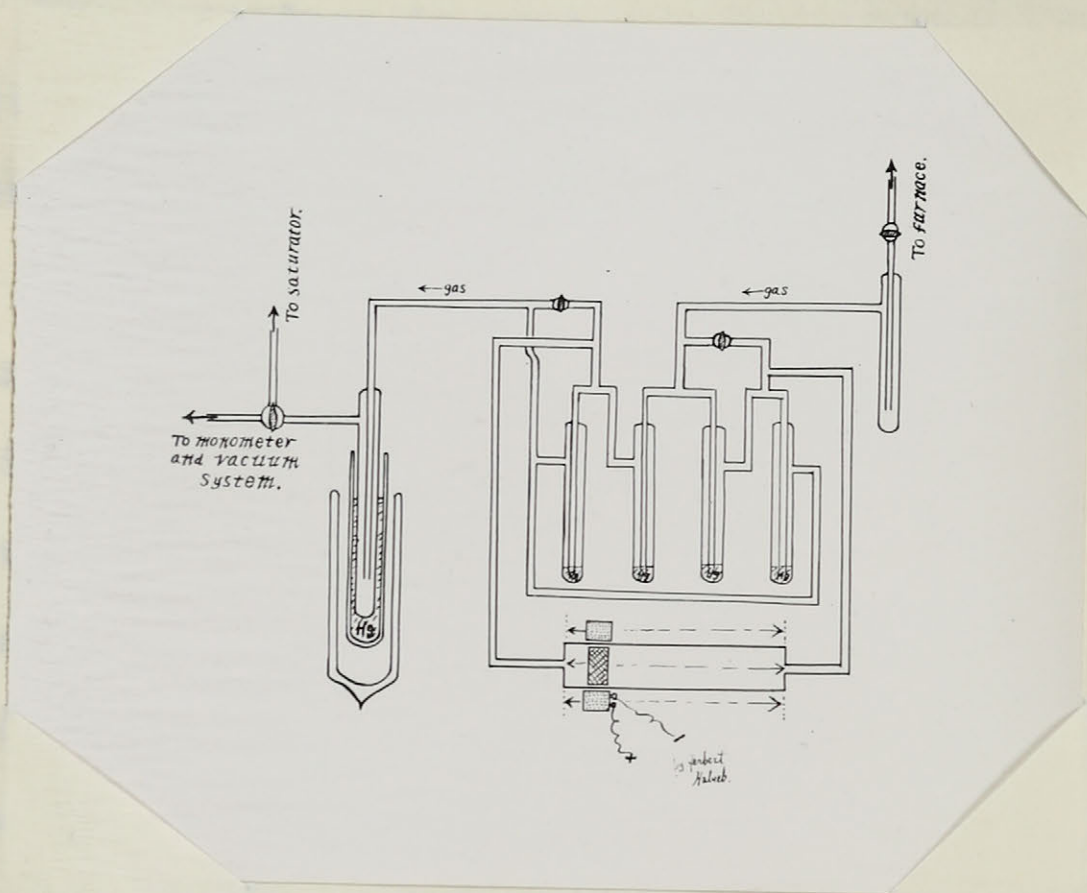suitable mechanical arrangment powered by a 1/4 horse-
power electric motor.

To saturator.

To monometer and vacuum System.

←gas

←gas

To furnace.

H₂

Figure VIII

The circulating part of the system .

The brass of the cylinder is joined to the glass of the apparatus by De Khotinsky joints - not shown in diagram. The circulation flow is about 1600 cc. of gas per minute .

The procedure in making a run is essentially that described for the static runs excepting the added care inherent in the circulating part of the system.

The trapping can be carried out with solid $C O_2$ and acetone to give a trapping temperature of $-79^{\circ}C$. or with liquid O_2 so applied that a trapping temperature of $-125^{\circ}C$. to $-130^{\circ}C$. can be maintained. This is accomplished by means of a double walled vessel containing mercury placed around the trap, old hack saw blades and iron wire may dip down into the mercury and inside the double walled vessel itself so that there is an added conduction of heat away into the air. Then a Dewar flask of liquid air is raised up around this to such a height that temperature equilibrium is reached at $-125^{\circ}C$. to $-130^{\circ}C.$, as indicated by the vapor pressure of the ethylene condensed in the trap, i.e. between 16 cm. and 9 cm. pressure. Once equilibrium had set in the trap required an addition of liquid air into the Dewar about every 20 minutes. The temperature oscillation was that equivalent to a C_2H_4 vapor pressure variation of from 9 to 16 cm.

Trapping at -125^OC should be fairly effective as the following table would suggest.

Compound	Temperature,^{O}C.	Vapor Pressure,mm.
Ethylene	-125	170
Propylene	"	4
Butylene	"	0.1

The runs made in the circulating system were primarily for the purpose of product identification and qualitative analysis. Quantitative analysis was not to be hoped for, considering the rapid deterioration of the lamps and the added complication of carbon or polymer $(CH_2)_n$ depositing on the inside of the reaction vessel especially on the wall closest to the resonance lamp.

The products of a run were analysed with a low temperature fractionating column of the Podbielniak type, the gaseous products being transfered from the reaction system to the column by means of a combined Toepler pump and gas holder. The gases were fractionated at a pressure of 76 cm.,and sometimes the pressure of fractionation was reduced to 30 cm. for the higher boiling fractions of C_4 and C_5 hydrocarbons.

The distillation pressure was maintained by having a scratched stopcock in between the still and the evacuated receiving vessel. The temperature at the head of

the column was measured by means of a fine copper - constantan thermocouple connected to a millivoltmeter (pyrometer). The thermocouple and pyrometer were calibrated by means of a known mixture of C_2H_4, CH_4, C_2H_6 and C_3H_8 .

By plotting the pressure in the receiving vessel against the temperature at the still head, a curve is obtained which shows the temperatures at which the product fractions distil over and the pressures at which the various products enter the receiving vessel. So knowing the volume of the vessel and the pressure exerted by a product in it, the mole percent of the product may be easily calculated. A typical analytical curve of this type is shown in figure IX . The section in which the distillation pressure was 76 cm. shows the C_2H_4 and C_3H_6 fractions, while the section at 30 cm. pressure shows the C_4 fraction, which is probably two isomers of butene plus a little C_5 that is not noticeble in this case.

The reaction products obtained in all cases were chiefly propylene and a C_4 hydrocarbon probably butene with an appreciable amount of higher hydrocarbons C_5 to C_8 .

Combustions on the propylene showed it to be a C_3 hydrocarbon; similarily with the C_4 hydrocarbon.

There is also a small amount of C_2H_2 and H_2 formed. The amount of hydrogen in a 400 cc. sample varied from 6 cm. to 20 cm. in a still volume of 15 cc.
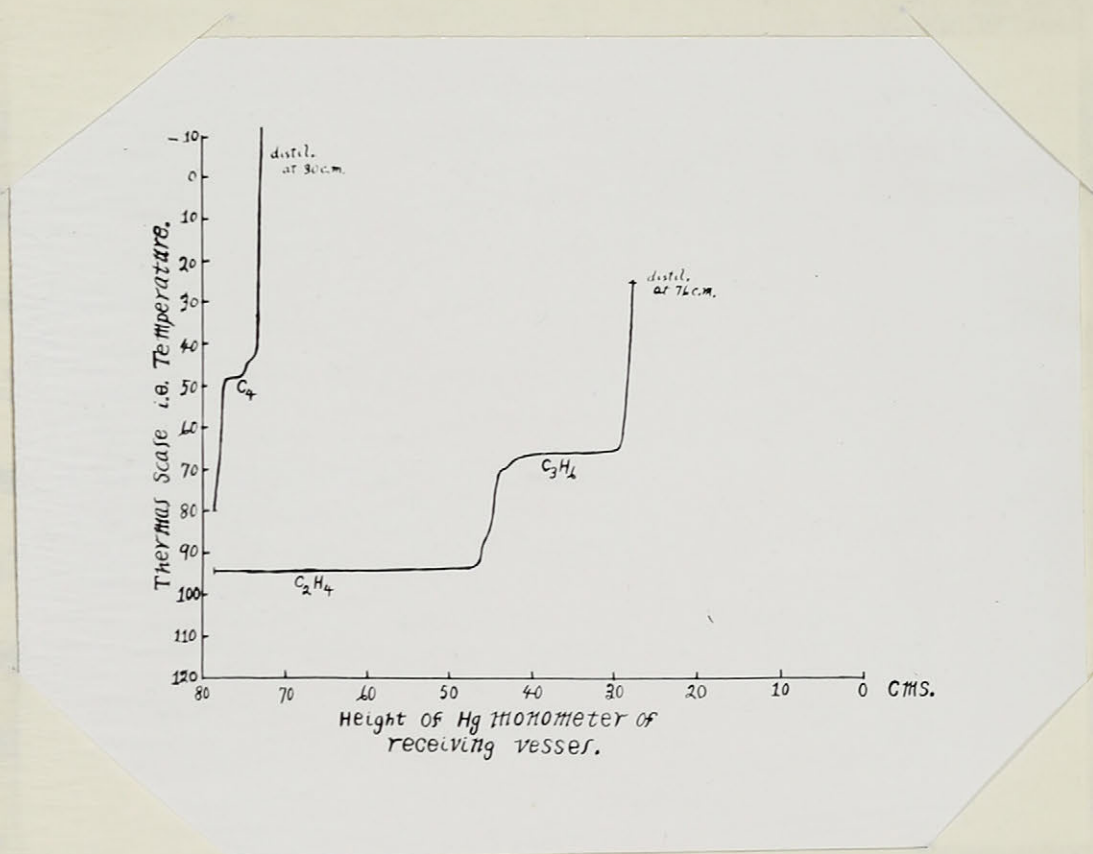
Figure IX

Distillation curve by a Podbielniak
low temperature column of the products
of a typical circulating run.

Combustions on this uncondensible hydrogen indicated that it was practically all H_2 and the 7% of C found in some cases was most likely due to a little C_2H_4 being trapped in the H_2.

In an average long run about o.1 cc. of liquid products was obtained for every 1000 cc. of gas, reactant and products combined.

All runs but two were made with the filters off; some were made with, and some without trapping. The runs with the filters on gave practically the same products as those without, but as expected the rate was slower.

Blanks on the C_2H_4 used indicated no detectable impurities. Thermal blanks in the presence of zinc vapor in one case gave a trace of C_3H_6 and in an other where there was continous circulation for 48 hours an appreciable amount of C_3H_6 was formed. The probable catalytic polymerization due to the possible presence of a little ZnO in the saturator is negligible as shown by blank runs.

The circulating runs were made at a temperature of $360^\circ \pm 15^\circ$ C.; this large variation of temperature being permissable as static runs indicated practically no change in the rate of the reaction over the temperature range indicated.

The products for all the runs are given in mole percent in the following table.

Table XVI

Effective volume of system: 1700 cc.

Circulating rate: 1600 cc./min.

Temperature of Furnaces: $360^{\circ}C$.

Zinc vapor pressure: 0.022 mm.

Lamp current: 110 m.a.

Run #	Gaseous products, mole %						Trapping	Corex-D filter	Time of run, hours
	C_2H_4	C_2H_2	C_3H_6	C_4	$C_5\&C_6$	H_2			
1	81.6		15.0	3.4		0.2	CO_2	yes	25
2	75.2		21.8	2.8		0.3	CO_2	no	11
3	82.7		14.3	2.9		0.2	CO_2	no	28
4	81.2		11.5	7.1		0.3	no	no	45
5	56.8		26.3	9.4	5.9	1.6	no	no	19
6	52.6		27.6	11.8	6.9	1,2	no	no	26
7	80.5	0.5	12.9	4.2	1.4	0.4	$-125^{\circ}C.$	no	10
8	84.0	0.3	10.8	3.5	1.2	0.3	"	nO	10
9	91.2	0.03	4.8	2.0	2.0	0.05	"	yes	20
10	92.7		7.1			0.2	no	(thermal blank)	48
11	99		1?		$\ll$0.2		no	" " " " " " "	an all week blank with 5min. circulat. every day

DISCUSSION

The zinc photosensitization of ethylene has shown that with the $Zn(4\,^3P_1)$ reonance state very little reaction was induced, but with the $Zn(4\,^1P_1)$ resonance state the reaction was much faster. Ethylene readily absorbs or 'quenches' the 2139Å resonance line but not the 3076Å line .
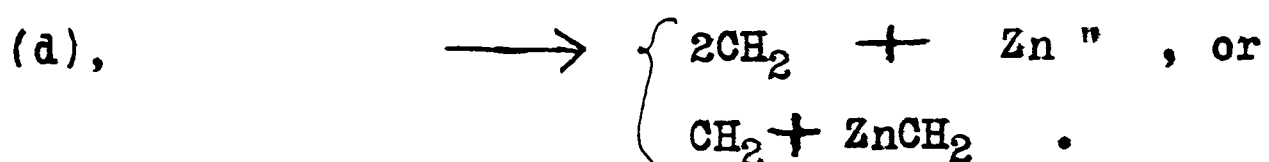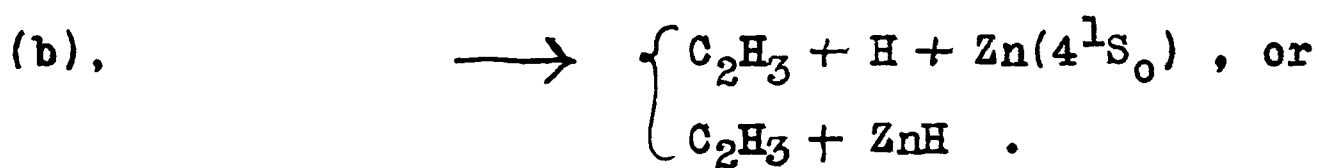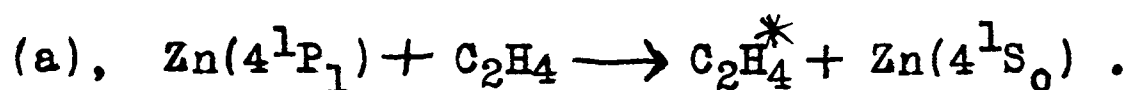
The main products of the reaction are in order of importance propylene, a C_4 hydrocarbon probably butene, some C_5 and higher hydrocarbons, plus a little hydrogen and acetylene. The essential difference between the results with zinc as compared with those obtained with mercury or cadmium in the analogous reaction is that here propylene is the most important product whereas the Hg and Cd cases have not indicated any production of propylene.

The explanation might be that the zinc sensitization has been carried out at a much higher temperature and reactions that do not go at the lower temperatures now may go; or that it is due to an inherent property of the zinc itself.

The present results are only a start in the investigation of zinc photosensitized reactions. On this account and on account of the experimental difficulties involved, it is too much to hope that a complete mechanism, proved at all stages, can be obtained.

Since the $Zn(4^3P_1)$ reaction is so slow and since what products do result are the same as in the $Zn(^1P_1)$ reaction, we can assume that the $Zn(4^3P_1)$ reaction is the same as the $Zn(^1P_1)$ reaction; but not as efficient since the $Zn(^3P_1)$ state has not the energy of the $Zn(^1P_1)$ state and will therefore induce reactions only in the more thermally energetic C_2H_4 molecules.

The possible primary reactions of $Zn(4^1P_1) + C_2H_4$ are :

(a), $Zn(4^1P_1) + C_2H_4 \longrightarrow C_2H_4^* + Zn(4^1S_0)$.

(b), $\longrightarrow \begin{cases} C_2H_3 + H + Zn(4^1S_0) \text{ , or} \\ C_2H_3 + ZnH \text{ .} \end{cases}$

(c), $\longrightarrow C_2H_2 + H_2 + Zn$ " .

(d), $\longrightarrow \begin{cases} 2CH_2 + Zn \text{ " , or} \\ CH_2 + ZnCH_2 \text{ .} \end{cases}$

There are a number of others which may be written, but which must be ruled out at once on energetic grounds, such as $\longrightarrow C_2H_2 + 2H$, etc .

(a) If (a) is the mechanism , the only possible secondary reactions are

$$C_2H_4^* + C_2H_4 \longrightarrow \text{products} ,$$

and

$$C_2H_4^* \longrightarrow \text{products} .$$
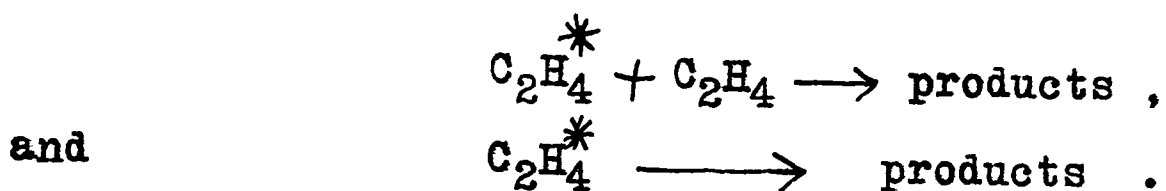
The latter can be neglected as the exclusive secondary reaction since it is indestinguishable from (b), (c) and (d). Both might occur. I.e. we might have

$$C_2H_4^* + C_2H_4 \longrightarrow C_4H_8 \quad , \text{ and}$$

sometimes, i.e. if the excited molecule does not collide soon enough it decomposes unimolecularly

$$C_2H_4^* \longrightarrow C_2H_2 + H_2 .$$
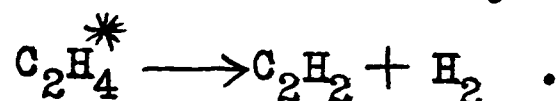
This would explain the formation mainly of butene, with some acetylene as in the case with the cadmium photosensitized reaction.

On this mechanism propylene would be formed by a secondary reaction of butene, which could still be excited, i.e.

$$C_2H_4^* + C_2H_4 \longrightarrow C_4H_8^* ,$$
$$C_4H_8^* \longrightarrow C_3H_6 + CH_2 ,$$
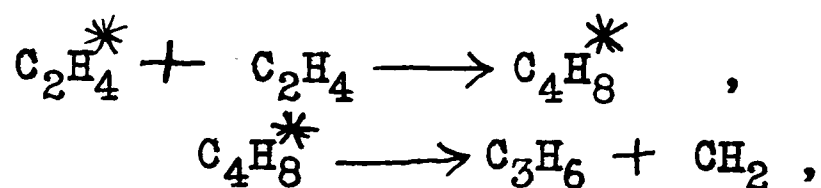
and

$$C_2H_4 + CH_2 \longrightarrow C_3H_6 \quad \text{is likely}$$

since the temperature is quite high.

Or butene could be decomposed, since it probably quenches strongly, by

$$C_4H_8 + Zn^* \longrightarrow C_3H_6 + CH_2 + Zn \quad \text{(but in}$$

spite of trapping at -125°C. C_3H_6 is still formed in the usual large amounts) ; or by a variety of ways involving radicals. These are discussed in more detail under (b) .

If this is the reaction mechanism, than we have the question, why should not the $Zn(4^3P_1)$ state be as efficient in exciting the C_2H_4 as the $Zn(4^1P_1)$ state? For the energy in the $Zn(4^3P_1)$ state is far above that necessary for the thermal reaction $2C_2H_4 \longrightarrow C_4H_8$.

The explanation might be in the concept of "Quantum mechanical resonance"; or it may be that an intermediate complex is readily formed by one state and not by the other, but opposing this is the fact that the $Zn(4^3P_1)$ state has a hundredfold longer life than the $Zn(4^1P_1)$ state.

(b) $\qquad C_2H_4 + Zn^* \longrightarrow C_2H_3 + H + Zn$

This is virtually the same as $\longrightarrow C_2H_3 + ZnH$ since the life of ZnH under the experimental conditions of this work is only $\sim 10^{-7}$ secs.

If this occurs than all the H atoms will immediately disappear by $\quad C_2H_4 + H \longrightarrow C_2H_5$ (fast) , and since C_2H_4 is in excess the other secondary reactions will of necessity be $\quad C_2H_3 + C_2H_4 \longrightarrow C_4H_7$, or

$$\longrightarrow C_2H_2 + C_2H_5 \quad , \text{ and}$$

$C_2H_4 + C_2H_5 \longrightarrow C_4H_9$ which obviously will give butylene thus

$$C_4H_9 \longrightarrow C_4H_8 + H \quad , \text{ and propylene}$$
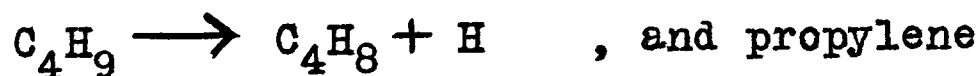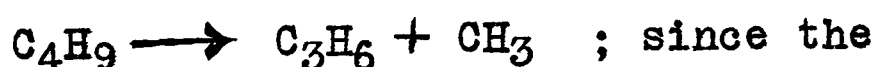
thus
$$C_4H_9 \longrightarrow C_3H_6 + CH_3 \quad ; \text{ since the}$$
butyl radical is definitely unstable at $360^{\circ}C$.

This mechanism appears to satisfy many of the requirements in both the zinc and cadmium reactions, excepting two difficulties; in the above mechanism hydrogen would not be produced but consumed, and in the Cd reaction no propylene is formed.

$$(c) \qquad C_2H_4 + Zn^{*} \longrightarrow C_2H_2 + H_2 + Zn$$

This reaction may occur to some extent, but appears to be unimportant here, since there is no initial pressure rise as in the mercury case, and as we have seen the amount of C_2H_2 formed is very small. Whereas in the mercury case, (c) is one of the important primary steps, and perhaps the only one. It must be the one in the mercury case since there is an initial pressure rise which seems to be proportional to the amount of C_2H_2 formed, as a matter of fact the initial products seem to be only H_2 and C_2H_2 and as much as 10% of C_2H_2 has been formed in the mercury reaction.

Thus the amounts of acetylene formed with Hg, Cd and Zn, suggest that (c) is of primary importance with Hg, of only moderate importance with Cd, and of only little importance with Zn .

It is interesting to note that it is the $Hg(6^3P_1)$ state that causes (c) to go, whereas the $Cd(^3P_1)$ state and the $Zn(^3P_1)$ state cause very little if any of (c) , while

the $Zn(^1P_1)$ state and the $Cd(^1P_1)$ state cause a little
of (c) but much more total reaction than can be accounted
for by (c). This suggests that the path of the reaction
is a function of the energy supplied and that there is
not just one definite mechanism but probably a number of
them of more or less importance depending on the specific
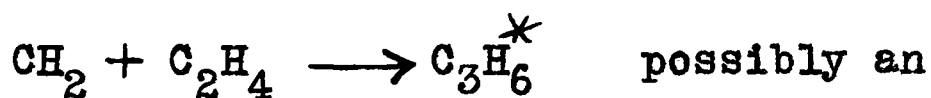case.

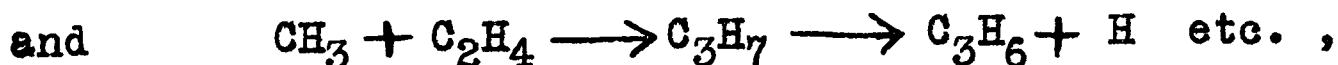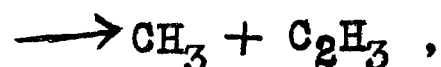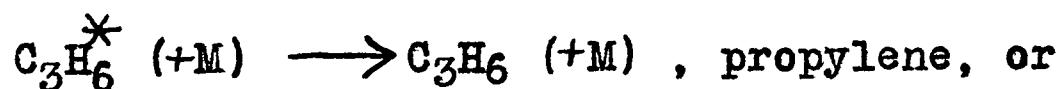$$\text{(d)} \qquad C_2H_4 + Zn^* \longrightarrow 2CH_2 + Zn$$

Regardless of primary mechanism,
i.e. $\longrightarrow ZnCH_2 + CH_2$ or otherwise , the net
result is the formation of $2CH_2$, which are most likely
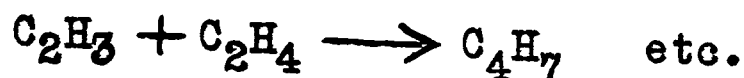molecules in which the C has a valency of two and
where $CH_2{=} \longrightarrow CH_2 + \underline{37}\ kcal.\ \underline{(90)}$.

Now because of the fairly high temperature
and excess of C_2H_4 the only practicable reaction of the
CH_2 is
$$CH_2 + C_2H_4 \longrightarrow C_3H_6^* \qquad \text{possibly an}$$

activated complex, which may then give

$$C_3H_6^* \ (+M) \longrightarrow C_3H_6 \ (+M) \ , \text{ propylene, or}$$

$$\longrightarrow C_2H_4 + CH_2 , \text{ or}$$

$$\longrightarrow CH_3 + C_2H_3 ,$$

and $\qquad CH_3 + C_2H_4 \longrightarrow C_3H_7 \longrightarrow C_3H_6 + H$ etc. ,

and
$$C_2H_3 + C_2H_4 \longrightarrow C_4H_7 \quad \text{etc.}$$

The large amount of propylene formation apparently favors this mechanism for the zinc reaction. But why propylene is not formed in the mercury and cadmium reactions must presuppose that the $Zn(4^1P_1)$ state has enough energy , 133.4 kcal., to split the $C=C$ bond whereas the $Hg(6^3P_1)$ state of 112.2 kcal., and the $Cd(5^1P_1)$ state of 124.4 kcal. have not; or that zinc can form a compound of the type $ZnCH_2$ whereas Hg and Cd do not.

In the static runs of $Zn^* + H_2 + C_2H_4$, from the rate of the reaction and from the analogous Cd and Hg reactions, it is plausible to assume that the initial step is
$$Zn^* + H_2 \longrightarrow 2H + Zn \quad \text{followed}$$
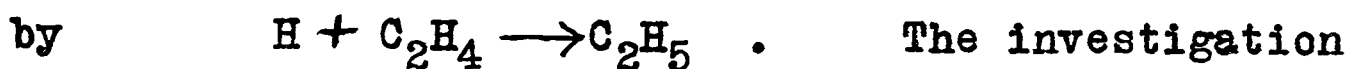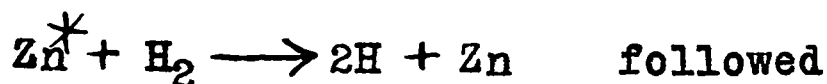
by
$$H + C_2H_4 \longrightarrow C_2H_5 \quad .$$
The investigation of this reaction in future work will be of great interest from the standpoint of what light it may throw upon the $Zn^* + C_2H_4$ reaction .
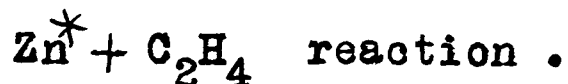
No chain processes need to be considered for the $Zn^* + C_2H_4$ reaction, since on the basis of a comparison of rates with those for cadmium the quantum yield appears to be probably somewhere in the range 0.1 to 0.5 .

In spite of obstacles, results warrant a continuation
of the work initiated here with the various hydrocarbons.

Both the subject of quenching and the spectro-
scopic investigation for such postulated molecules as
ZnH and ZnCH$_2$ are desirable future works; especially the
spectroscopic determination of the hydride, since it has
been a necessary assumption in the Cd(5^3P$_1$) reactions
with ethane and propane .

Since no previous work on zinc photosensitization
had been done, this work was necessarily exploratory and
although having shown considerable possibilities leaves
much yet to be done.

SUMMARY AND CONTRIBUTION TO KNOWLEDGE

A satisfactory zinc resonance lamp has been developed that possess a working temperature range of 320 to 420°C. and emits both of the resonance lines 3076Å and 2139Å; the former being about 2 to 5 times as intense as the latter.

The technique for zinc photosensitization using the $Zn(4^3P_1)$ state alone, and with the $Zn(4^1P_1)$ state has been developed.

The photosensitized reactions of ethylene with $Zn(4^3P_1)$, and with $Zn(4^1P_1)$ have been investigated. The products in both cases appear to be the same, and are chiefly propylene and a C_4 hydrocarbon probably butene, with some higher hydrocarbons and a little acetylene and hydrogen.

The rate of polymerization induced in C_2H_4 by $Zn(4^3P_1)$ plus $Zn(4^1P_1)$ is ten times as great as that induced by the $Zn(4^3P_1)$ alone.

The primary mechanism is probably one or both of the following

$$C_2H_4 + Zn(excited) \longrightarrow C_2H_3 + H + Zn \text{ , or}$$

$$C_2H_4 + Zn(excited) \longrightarrow 2CH_2 + Zn \text{ .}$$
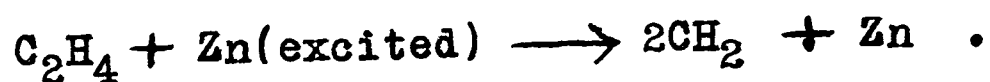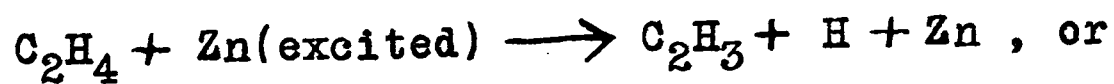
Both of these with plausible secondary reactions give rise to the products obtained.

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