CADMIUM PHOTOSENSITIZED REACTIONS.

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CONTENTS

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INTRODUCTION.

Paralleling the developments in the study of atomic reactions by the discharge tube method (1-4), photochemistry has greatly contributed to the proper understanding of thermal reaction mechanism. Indeed, photochemical methods offer a powerful means of investigating the problems of the interaction of light and matter thus giving an insight into the behavior of individual atoms, radicals and molecules. However, thermal and photochemical processes are closely correlated, the secondary steps in photochemical reactions being properly thermal reactions. Of course, they differ in their primary steps, the activation mechanism involving activation by collision in the case of thermal decomposition and light absorption in the other case.

Photosensitization.

As only the light which is absorbed can cause a chemical reaction to occur, it is obvious that beyond a certain maximum wave-length where absorption is nil, no photolysis will take place. This maximum wave-length, the photochemical threshold, coincides in many cases with the beginning of a conti-

nuum or a predissociation region (corresponding to an adiabatic transition from an attractive state to a repulsive or weakly attractive state)(5). To provoke a reaction in molecules transparent to light of a certain wave-length it is therefore necessary to add a substance capable of absorbing light energy at this wave-length and conveying it to the reactant molecules without being itself permanently transformed. This process is known as photosensitization. It may find useful applications in the solid and liquid phases but theoretically it is studied with more advantage in the gaseous phase.

The present work deals with cadmium photosensitization in the gaseous phase, using the cadmium resonance radiation as source of excitation. Consequently, prior to any discussion on the absorption and transfer of light to the reactant molecules, it is important to discuss briefly the emission spectrum of cadmium.

In this discussion, it is convenient to make a Grotrian diagram connecting the energy of various states with the quantum number of these states. Cadmium has two electrons in its outer shell and will therefore possess singlet and triplet systems. The combination principle along with the selection rules will give a number of permissible transitions the most important of which are shown in figure I. The two lines connecting the ground state 5^1S_0 to the 5^1P_1 and 5^3P_1 states respecti-

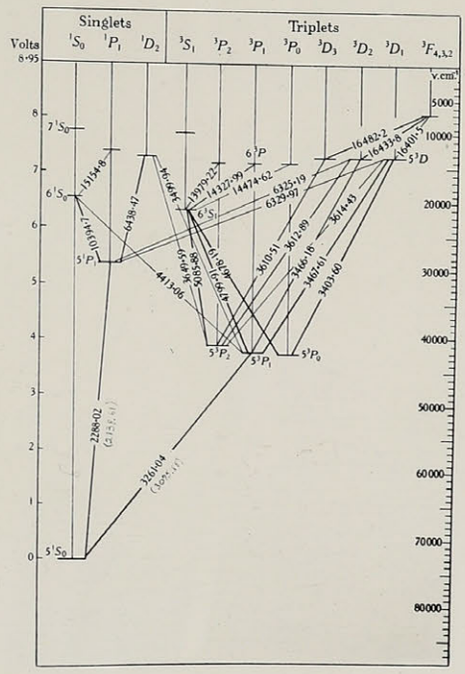


Figure I

Energy levels of cadmium . Cf.(13).

vely correspond to the two resonance lines of cadmium. In the present work only the $5^1S_0 - 5^3P_1$ line (87 Kcal.) is considered. The transitions between the 5^3P_0 and 5^3P_2 metastable states 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.

It is to be noted that the energy difference between the 5^3P_0 and 5^3P_1 is small (only 0.07 volt) compared to that of mercury for the same transition (0.21 volt). The collision of an excited cadmium atom in the 5^3P_0 with a molecule containing a relatively small amount of kinetic energy will therefore be sufficient to raise it to the 5^3P_1 level. The first zinc resonance line is at 92 Kcal. as shown in brackets on the Grotrian diagram.

Excitation of the Cadmium Atoms.

According to the quantum theory, the absorption of light produces a change from a lower level to a higher one. It is obvious that the line spectrum of absorption of an atom will be much simpler than the emission spectrum because at the temperatures used in the study of photosensitized reactions the great majority of the atoms before excitation will be present in the normal state and will therefore undergo only a few types of transi-

tions to an appreciable extent. Indeed, information regarding such distribution of molecules among the various possible energy states is given by the following equation:

$$\frac{n_i}{n_N} = \frac{p_i}{p_N} \; e^{-(E_i - E_N)/RT}$$

where n_i and n_N are the number of molecules in the i^{th} and in the normal states respectively; p_i and p_N the statistical weigths of these states; $E_i - E_N$ the difference of energy per mole from the i^{th} to the normal state.

The process by which light energy is taken by the cadmium atom to convert it into an excited atom may be conveniently schematised by the following equation:

$$Cd(5^1S_o) + h\nu\ (3261\ \text{Å}) \longrightarrow Cd(5^3P_1)$$

This process for cadmium was studied by Terenin (82) and Solleillet (84). In a mathematical treatment of the subject, Milne (6) has shown on the basis of Einstein's radiation theory 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. The efficiency of process (1) will depend largely therefore on the distribution of intensities of the exciting and absorption lines.

Figure II, gives the intensity of the resonance radiation plotted against the frequency. Since in the actual construction of a resonance source the discharge carrier gas is at a few millimetres pressure, the resonance line emitted has an appreciable breadth due specially to pressure broadening (as shown by A). On the contrary, when the vapor pressure is low in the absorption cell, a narrow absorption line is found (as shown by B). It is obvious in that case that the absorption will be incomplete, all the portion of the emission radiation represented by the area outside B being lost. However, in the presence of a foreign gas, the pressure broadening effect will become appreciable in the absorption cell. At a certain pressure the breadth of the emission line and that of the absorption line will coincide and the absorption will be complete (ideal case). At higher pressures, the absorption line will become still broader as shown in C. The area in common indicates the degree of absorption and therefore the rate at which excited atoms are formed.

When no foreign gas is present, the inverse process of (1) becomes very efficient:

$$Cd(5^3P_1) \longrightarrow h\nu\ (\lambda = 3261\ \text{Å}) + Cd(5^1S_0). \quad (2)$$

This transition from the 5^3P_1 to the ground state gives rise to light quanta of a definite frequency, which is properly the resonance radiation.

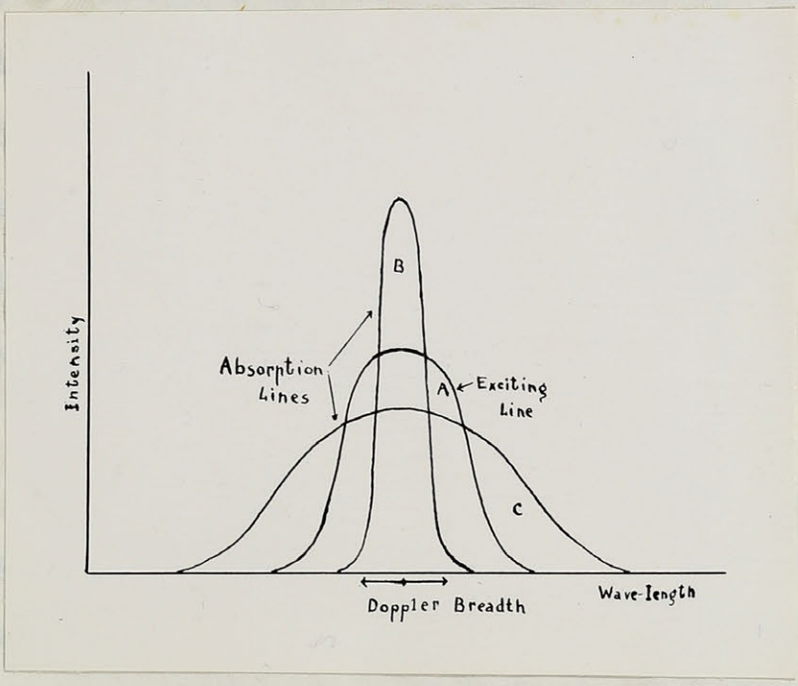


Figure II

Exciting and Absorption Lines.

Energy Transfer.

In the presence of a foreign gas, the situation is more complicated. Depending on the lifetime and nature of the excited atom and the number of foreign molecules present, deactivation will proceed through collisions of the second kind. Therefore only a fraction of the activated atoms will undergo process (2) and the intensity of the resonance line will be proportionally decreased. This is the quenching phenomenon. Its efficiency determines the extent to which the excited atoms are releasing their energy to the foreign gas molecules and thus often bringing them into in a reactive state.

Extensive studies of the quenching of mercury by foreign gases have been made by Wood (7), Stewart (8), Zemansky (9) and Bates (10). The following table gives the effective cross sections of hydrogen and a number of hydrocarbons:

Gas	Effective cross sections $\sigma_Q^2 \times 10^{16}$ cm^2.
Hydrogen	8.60
Methane	0.085
Ethane	0.594
Propane-	2.32
Butane	5.88

The quenching of optically excited cadmium atoms by foreign gases was first investigated qualitatively by Bates (11). He found that hydrogen was very effective in quenching the cadmium resonance radiation and suggested that it took up the energy of excitation as vibrational energy (hydrogen has a vibrational level at about 88 Kcal.).

P. Bender (12) radiated a mixture of hydrogen and cadmium vapor at 260°C. with light from a hydrogen-cadmium discharge tube. By means of a small Hilger spectrograph, he noticed that the resonance line was nearly all extinguished at 4 mm. of hydrogen. He explained the quenching by the formation of a normal cadmium hydride molecule and a hydrogen atom resulting from the collision between the excited 5^3P_1 cadmium atom and a hydrogen molecule, as shown in the following energetically balanced equation:

$$Cd + H_2 \longrightarrow CdH + H + 88 \text{ Kcal.}$$

taking the approximate value of 15.5 Kcal. calculated by Svensson (86) for the heat of formation of cadmium hydride. The energy discrepancy in that case would be only 0.013 volt. A further evidence to the formation of normal CdH was put forth by obtaining the CdH band system through excitation with light from a hydrogen-cadmium discharge lamp. Recently Olsen has also investigated the optical excitation of cadmium deuteride CdD (12a).

The addition of nitrogen and carbon monoxide produced a notable increase in the intensity of the 3404 Å line (2 to 1) starting at 0.01 mm. and reaching a maximum at 0.1 mm. and then persisting throughout the whole range of pressures observed. This was explained by an increase in the population of the atoms in the 5^3P_o metastable state. There appeared however to be no enhancement of the visible triplet ($6^3S_1 - 5^3P$).

Recently Lipson and Mitchell (13) investigated in a quantitative way the quenching of optically excited cadmium atoms by foreign gases. Unfortunately, as seen in the table below, they studied only one hydrocarbon: methane.

Gas	Effective cross sections $\sigma_q^2 \times 10^{16}$ cm^2	Quenching to half value
Hydrogen	0.67	0.4 mm.
Deuterium	0.19	
CO	0.14	
NH_3	0.041	
N_2	0.021	
CH_4	0.012	60 mm.

On the basis of the Stern-Volmer formula and of the Maxwellian distribution of velocities, they calculated

the following quantitative relation between the quenching Q and the effective cross section σ_Q^2 :

$$\sigma_Q^2 = \frac{1/Q.p}{\tau\ 2666.6\ \left[\ 2\pi N/kT\ (1/M_1 \quad 1/M_2)\ \right]^{\frac{1}{2}}}$$

where p is the pressure in mm. of mercury; τ is the mean life of $Cd(5^3P_1)$ 2.5×10^{-6} sec. (99-100-101); M_1 and M_2 are the molecular weights of the colliding particles; N the molecular concentration and k is the universal gas constant per molecule (13).

As no data were obtainable on the quenching of cadmium resonance radiation by hydrocarbons other than methane, absorption of the resonance radiation by foreign gases in the presence of cadmium vapor had to be measured directly under the same conditions as that of the photosensitized reactions. The values obtained in these measurements are not to be considered as true quenching values as will be shown by a short consideration of figure II giving the relation between the broad exciting line and the various kinds of absorption lines as met with under the actual experimental conditions. The areas which are in common, as already mentioned, are indicative of the energy absorbed by the foreign gas. As the line becomes broader on addition of the foreign gas (pressure broadening) the absorption is increased (case B) and the real quenching is partly or completely offset. Furthermore, the present absorption measurements were

performed at a cadmium pressure of 0.018 mm. which is far from being the ideal condition but was required for the proper operation of the light source. Such a pressure may give rise to a considerable diffusion of the imprisoned radiation thus altering the quenching values. It may affect also the photosensitized reaction by the fact that most of the effective deactivation collisions would occur near the walls of the lamp, hence favouring the recombination of atomic hydrogen and that of radicals on the walls. However, the actual absorption values thus obtained are quite satisfactory to calculate the quantum yield and to give a comparison between the hydrocarbons studied as to what their relative efficiencies are as deactivators of the excited cadmium atoms.

A general principle of fundamental importance can be applied in the adequate interpretation of the interchange of the excitation energy during quenching. The efficiency of a deactivator is based primarily on its own value as acceptor of the energy coming into play, in other words the smaller the energy that must be converted into kinetic energy, the greater the probability of deactivation. Hence, the most probable transfer in a collision of the second kind is the one which involves the least energy conversion into kinetic energy (14). When a simple molecule is put into a reactive state by a collision of the second kind, it is possible to infer to a certain extent the strength of the ruptured bond on the theoretical

grounds that quenching will become an efficient process only when there is a high degree of resonance between the excited atom and the deactivator. Photosensitization is therefore a tool by which a definite amount of energy can be furnished to the reactant molecules.

This general method was first applied successfully to the investigation of mercury photosensitized reactions. In the case of organic decompositions, free radicals are usually produced in the process and it therefore gives results of special interest in connection with the rates of elementary reactions.

A wide variety of reactions are possible by the transfer of the $Hg(6^3P_1)$ excitation energy (112 Kcal.) to simple hydrocarbon molecule but there are only three main possible primary steps:

a) the rupture of a C-C bond,

b) the rupture of a C-H bond,

c) the dissociation into atoms of the hydrogen resulting from b).

These processes require respectively about 70-80 Kcal., 90-100 Kcal., and 103 Kcal.

The great efficiency of the mercury sensitized dissociation of hydrogen affords a simple method of studying quantita-

tively the reactions of atomic hydrogen. Cario and Frank (17) were the promoters of this method which has been used extensively.

A schematic illustration of the main possible steps of the mercury photosensitized reaction follows:

(1) $Hg(6^1S_0) + h\nu\ (\lambda = 2537\ \text{Å}) \longrightarrow Hg(6^3P_1)$

(2) $Hg(6^3P_1) + H_2 \longrightarrow HgH + H$

(3) $H + X \longrightarrow$ Products

(4) $2H + M \longrightarrow H_2 + M$

where M is a third body.

Though necessitating a larger amount of conversion into kinetic energy, the occurence of reaction (2) is shown to occur by the presence of HgH during the reaction. Furthermore, the possibility of the reaction

$$Hg(6^3P_1) + H_2 \longrightarrow H + H + Hg(6^1S_0)$$

is questionable on the basis of the principle of microscopical reversibility, the inverse reaction actually involving a three body collision.

Knowing the intensity of illumination and the rate of recombination of hydrogen atoms, the velocity constant of (3) can be calculated (18-19). It thus affords a very convenient method of studying the reactions of atomic hydrogen.

Considering the importance of the information which has been derived from mercury photosensitized experiments, it is of great interest to investigate other photosensitized reactions involving a smaller amount of energy. Quite a number of metals offer sufficiently high vapor pressures at moderate temperatures to give convenient sources of resonance radiation. Among these are specially potassium, sodium, cadmium and zinc.

Experiments were conducted by Jungers and Taylor (20) on sodium photosensitized reactions. They found that even though the sodium fluorescence was completely extinguished no chemical reaction could be detected by exposing ethylene to the action of the excited sodium atoms (48 Kcal.).

On the other hand, cadmium and zinc with the $^3P_1$ levels at 87 Kcal. and 92 Kcal. above the normal state respectively, offer a new field of possibilities with great theoretical significance.

Bates and Taylor (30) were the first to investigate the cadmium photosensitized reactions of hydrogen-ethylene. Their source of cadmium resonance radiation was of the Cooper-Hewitt type. After exposing for a long time a mixture of ethylene and hydrogen to optically excited cadmium atoms, at 260°C., they noticed a notable drop in pressure. Mainly on theoretical grounds they concluded that only polymerisation

occurred since the cadmium photosensitized formation of hydrogen atoms from hydrogen could not be the primary process, the dissociation of hydrogen being 103 Kcal. viz. about 16 Kcal. in excess of the energy available from the $Cd(5^3P_1)$. No other work on cadmium photosensitized reactions is reported.

Working in a parallel field, Steacie and Habeeb (21) have recently developed an intense source of zinc resonance radiation and extensive work on zinc photosensitized reactions is intended.

The present investigation deals mainly with the cadmium photosensitized reactions of hydrocarbons which should be of interest by comparison with the corresponding action of optically excited mercury on the same gases. A short review of the previous work on photochemical and photosensitized reactions of the simple aliphatic hydrocarbons is therefore given:

Methane.

Methane has a continuous absorption region below 1800 Å. Leighton and Steiner (103) have investigated the photolysis of methane using a hydrogen discharge tube as light source. They reported a quantum efficiency in the order of unity. Groth (104) using a Harteck Xenon lamp found hydrogen and acetylene as the main decomposition products. The primary

reaction would be

$$CH_4 + h\nu \ (\lambda = 1469 \text{ and } 1295 \text{ Å}) \longrightarrow CH_3 + H$$

Recent investigations(54) on the mercury photosensitized decomposition of methane have shown a very small quantum yield at a temperature of 195°C., increasing rapidly to 0.25 at 350°C.

Ethane.

Direct photochemical decomposition of ethane at a wave-length of about 1850 Å showed formation of hydrogen and unsaturates (22).

While investigating the mercury photosensitized reaction of a hydrogen-ethylene mixture, Taylor and Hill (23) noticed anomalous pressure changes after the hydrogen-ethylene reaction was over. They suggested that a secondary reaction was taking place, the ethane formed by the hydrogenation of ethylene being attacked both by hydrogen atoms and optically excited mercury atoms. This led the path to a systematic investigation of the mercury photosensitized decomposition of ethane.

Kemula, Mrazek and Tolloczko (24) in their study of the ethane decomposition circulated the reaction mixture through a trap at -80°C. to remove the products of higher

molecular weight as fast as formed to reduce secondary processes. They observed that the decrease in pressure was followed by an increase in the amount of the liquid condensate formed. The gaseous products were found to be chiefly hydrogen and methane. The ratio of hydrogen to methane was increased with a higher trapping temperature. The liquid products consisted of butane, hexane and octane. To explain the formation of methane they suggested a mechanism involving a C-H bond rupture and the subsequent attack of ethane by the atomic hydrogen thus formed to give methane and methyl radicals.

The following scheme was suggested:

$$C_2H_6 + Hg(6^3P_1) \longrightarrow C_2H_6^* + Hg(6^1S_0)$$

$$C_2H_6^* \longrightarrow C_2H_5 + H$$

$$2\ C_2H_5 + M \longrightarrow C_4H_{10} + M$$

$$2\ H + M \longrightarrow H_2 + M$$

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

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

Octane formation was interpreted on the bases of butane decomposition:

$$C_4H_{10} \longrightarrow C_4H_9 + H$$

$$2\ C_4H_9 + M \longrightarrow C_8H_{18} + M$$

where M is a third body.

Steacie and Phillips (26) made a more complete inves-

tigation of the mercury photodecomposition of ethane. They observed the reaction both in a circulatory system (78) and a continuous flow system (26).

In the circulatory system, it was found by improved trapping methods that it is possible to remove entirely butane from the system as soon as formed, thus preventing the formation of secondary products. Under these circumstances the products of the reaction consisted of methane, propane and butane. The hydrogen formed was reported as the product of the decomposition of propane and butane. The suggested mechanism follows:

$$C_2H_6 + Hg(6^3P_1) \longrightarrow 2\ CH_3 + Hg(6^1S_0)$$

$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$$

$$2\ CH_3 \longrightarrow C_2H_6$$

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

$$CH_3 + C_2H_5 \longrightarrow C_3H_8$$

Another investigation of the mercury photosensitized decomposition of ethane has been made recently by Steacie and Phillips (26), a continuous flow system being used. They found a considerable production of hydrogen and concluded that the primary step in the reaction was a C-H bond rupture. The experiments were conducted at temperatures of 65°C., 90°C. and 450°C. The rate of formation of hydrogen increased with temperature. The following mechanism was suggested:

$$C_2H_6 + Hg(6^3P_1) \longrightarrow C_2H_5 + H + Hg(6^1S_0)$$
$$H_2 + Hg(6^3P_1) \longrightarrow 2\,H + Hg(6^1S_0)$$
$$H + C_2H_6 \longrightarrow CH_4 + CH_3$$
$$H + C_2H_6 \longrightarrow C_2H_5 + H_2$$
$$2\,CH_3 \longrightarrow C_2H_6$$
$$CH_3 + C_2H_5 \longrightarrow C_3H_8$$
$$2\,C_2H_5 \longrightarrow C_4H_{10}$$
$$2\,H \longrightarrow H_2$$

All this mechanism is based on the assumed large efficiency of the intermediary step producing methane and methyl radicals:

$$C_2H_6 + H \longrightarrow CH_4 + CH_3 \qquad (a)$$

It accounts satisfactorily for the various products found in the actual experiments provided that it is assumed that the disproportionation reaction (a) is about four times faster than reaction

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

As shown in a recent paper of Steacie and Parlee (89) this assumption is not compatible with the Rice-Herzfeld (27) mechanism for the thermal decomposition of ethane.

According to the Rice-Herzfeld mechanism the main steps in the decomposition of ethane are as follow:

		Activation Energy.
(1)	$C_2H_6 \longrightarrow 2\ CH_3$	80 Kcal.
(2)	$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$	20 "
(3)	$C_2H_5 \longrightarrow C_2H_4 + H$	49 "
(4)	$H + C_2H_6 \longrightarrow H_2 + C_2H_5$	17 "
(5)	$2\ H \longrightarrow H_2$	Triple collision
(6)	$H + C_2H_5 \longrightarrow C_2H_4 + H_2$	Small
	or C_2H_6	"
(7)	$H + CH_3 \longrightarrow CH_4$	"
(8)	$CH_3 + C_2H_5 \longrightarrow C_3H_8$	8 Kcal.
(9)	$2\ C_2H_5 \longrightarrow C_4H_{10}$	8 "

The activation energies given for the different steps are based partially on experimental data and partially assigned by Rice and Herzfeld to make the scheme agree with experiment. Neglecting the activation energies of (5), (7), (8) and (9) the overall activation energy would be:

$$E_{overall} = \tfrac{1}{2}\left[E_1 + E_3 + E_4 - E_6\right] = \quad 73 \text{ Kcal.}$$

in agreement with the measurements of Marek and McCluer (29). The overall rate of the scheme may be expressed by the relation:

$$-\frac{d}{dt}\left[C_2H_6\right] = \left[\frac{K_1\ K_3\ K_4}{2\ K_6}\right]^{1/2}\left[C_2H_6\right]$$

i.e. the reaction is of the first order. This was confirmed experimentally. Assuming as a reasonable approximation the value $10^{14}\ e^{-E/RT}$ as rate constant of the first order reactions

and $10^9 \ e^{-E/RT}$ as rate constant of bimolecular reactions, Rice and Herzfeld evaluated the rate constant for the separate steps and for the overall decomposition and found for this last value:

$$\log_{10} K = 15.1 - \frac{15,970}{T} \quad sec^{-1}.$$

Considerable doubt as to the validity of this mechanism resulted from the work of Patat and Sachsse (25). Using the ortho-para hydrogen conversion to measure the hydrogen atom concentration they found that it should be several powers of 10 lower than that calculated from the free radical chain theory (16).

The new value of E_4 (6.3 Kcal.) found by Steacie and Phillips (54) removed the disagreement between Patat and Sachsse's results and the Rice and Herzfeld scheme as regard to the hydrogen atom concentration, but it altered the value of the activation energy of the overall reaction.

Actually all the Rice (28) mechanisms are based on the high efficiency of reactions of the type

$$R + HX \longrightarrow RH + X$$

and on the low efficiency of the chain breaking disproportionation reactions of the type

$$R + CH_3(CH_2)_nCH_3 \longrightarrow RCH_3 + CH_3(CH_2)_n$$

Hence, the assumption that the intermediary disproportionation reaction

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

occurs to an appreciable extent in the mercury photosensitized decomposition of ethane would be entirely in disagreement with the fundamental idea of the Rice and Herzfeld scheme. Recently Taylor has suggested the possibility of the reaction

$$H + C_2H_5 \longrightarrow 2\ CH_3 \qquad (a)$$

as the main intermediary step in this decomposition. Recent experiments by Steacie and Parlee (89) on the reaction of hydrogen atoms with propane by the Wood-Bonhoeffer method offered strong evidence that reaction (a) occurred readily at room temperature.

Propane and Butane.

Very little work has been done on the photochemical reactions of the higher alkanes.

Recently Kemula and Dyduszynski (105) found hydrogen and unsaturated compounds as the result of the photolysis of propane and butane at a wave-length of 1850 Å.

Comparing the mercury photosensitized reactions of ethane, propane and butane, Taylor and Hill (23) observed that the rate of reaction with atomic hydrogen increased with the complexity of the molecule. Steacie and Phillips (78) made a preliminary investigation on the mercury photosensitized decomposition of butane and found that hydrogen was formed.

CADMIUM PHOTOSENSITIZED REACTIONS.

EXPERIMENTAL.

A satisfactory study of photosensitized reactions is based on a few experimental conditions, chiefly on the quality of the source of resonance radiation, on the transfer of this radiation energy to the reactants, on the purity of the materials under investigation, and finally on the method of analysis of the products.

Source of Resonance Radiation.

The source of resonance radiation must be intense enough so that the time required for a measurable amount of reaction will not be too long. The source of resonance radiation must also be free from any other radiation which could be directly or indirectly absorbed by the gases giving rise to a photochemical reaction which would alter the rate of the reaction under investigation to a certain extent. It is essential that the exciting light be unreversed. The effect of the motions and interactions of the atoms is to produce a spectral line whose intensity will be distributed over a range of wave-lengths giving the width proper of the line. The portion in the middle, called the centre of the line, should be more intense than the edges in case of unreversed light. Finally, the source of resonance radiation must be steady to give reproducible results.

Transfer of Light Energy.

In photosensitized reactions, this transfer of energy is made through the medium of a metal vapor which is raised to an upper excited state by the impinging quantum. The conditions must therefore be such that the maximum number of quanta is utilized. This is brought about by a proper geometrical design of the reaction cell and, also by a suitable vapor pressure of the admixed metal.

Purity of Materials.

Materials under investigation must be as pure as possible and great care must be taken in mixing known quantities of gases, to avoid errors due especially to back diffusion. Thus mixtures of definite known values may be obtained.

Method of Analysis.

The method of analysis must be sensitive and precise so as to estimate even small amount of the products formed during the reaction. Photosensitized reactions may be studied in the solid, the liquid and the gaseous phase. Though they may find many actual useful applications in the solid and liquid phases, they can be investigated more thoroughly and more advantageously in the gaseous phase. In this work only the reactions in the gaseous state are considered.

Consequently the method of analysis must be adapted specially to gas mixtures.

Source of Cadmium Resonance Radiation.

Although the properties of cadmium makes it very promissing in photochemistry, very little work has been done in this field (30). This is mainly due to the lack of a convenient source of reasonably high intensity in the cadmium resonance line at 3261 Å. This is not the least surprising, considering how the development of mercury photosensitization technique was considerably delayed through the lack of a suitable mercury lamp. Very convenient mercury arcs however were developed in the last ten years by the use of a stationary foreign gas.

In such lamps, the ions, electrons and metastable atoms present in the inert gas during the discharge will transfer by collisions the greater part of their energy to the admixed metallic vapor. The quantum condition restricts the amount of energy which the metal atom may accept to raise it to an excited state where it can reemit this energy as light as it reverts to its normal state. The process is so effective that the spectral lines emitted belong almost exclusively to the metallic vapor. This fact is remarkable especially if we consider the low concentration of metallic vapor present in a discharge tube compared to that of the inert gas. It can be explained advantageously by the following example. In a neon

discharge tube (neon pressure of 10mm.) containing cadmium at 250°C., the ratio of pressures indicates that there are about 2000 neon atoms for every cadmium atom. The excitation energy of neon is 16.6 volts, that of cadmium (5^3P_1) is 3.78 volts. Hence on applying the voltage to such a lamp, an electron emitted from the cathode will lose energy at first by impacts with the neon atoms untill it gets down to an energy lower than 16.6 volts whence it cannot excite directly the neon. Then it still has plenty of energy to excite the rare cadmium atoms, and cadmium light soon overshadows the neon's light. The inert gas will thus have two functions. It will furnish a path for the start of the discharge when the voltage is first applied, and, in some cases it will raise the temperature of the discharge tube to a value sufficient for the good performance of the source.

A number of lamps have been used in the past for the production of cadmium resonance radiation, neon or any other inert gases being used as carrier (31-38, 40-46, 48) of the discharge. Most of these however, are either weak or unsteady, or else, as in the case of the arcs with a circulating foreign gas are expensive, complicated and require too much attention to be convenient for photochemical purposes where long exposures are necessary.

In lamps using metals of high boiling point, great

difficulty is experienced in having a suitable pressure of the metallic vapor. Kunze (34) and Houtermans (33) solved this difficulty by placing the material whose vapor was to be mixed with the foreign gas in a side tube separately heated. This gave rise to condensation on the walls of the discharge tube thus extinguishing a part of the light. This could be partly avoided by running the arc at a high current with a consequent broadening of the lines.

By applying to the metal vapor an alternating potential from an oscillator at a frequency of the order of 10^8 cycles per second corresponding to 3-10 metres an electrodeless discharge has been obtained by Fairbrother and Tuck (38). At such a frequency, a discharge can be maintained in a gas at a very low pressure with the advantage that the only necessary electrode may be outside the tube containing the vapor. The only disadvantage of these electrodeless metal vapor lamps is the complicated set up and rather low intensity. They give a resonance line practically free from self-absorption.

The chief cause of self-absorption is a thick layer of the metallic vapor in the path of the light. The problem is thus to reduce to a minimum the condensation on the walls of the lamp. This was achieved by Cario-Lochte-Holtgreven (31) by the use of a circulating foreign gas which

would carry the electrical discharge and at the same time sweep away the excess of metal preventing it from condensing on the exit window. However, such lamps have the disadvantages of being quite complicated and having a relatively small exit window (51).

To obviate these disadvantages, it was thought that the nearly ideal conditions of the Cario-Lochte-Holtgreven lamp could be duplicated in a lamp where the metal vapor, instead of the inert gas, would have a constant flow from one electrode to the other. As it will be seen later, this was achieved by an extremely simple device.

Cadmium and zinc have appreciable vapor pressures at sufficiently low temperatures as can be seen from the following table. For comparison a few data are also given for mercury.

Temperature	Zinc At. No. 30	Cadmium At. No. 48	Mercury At. No. 80
		Pressure in mm.	
25°C.			0.0018
219.1		0.001	
230.		0.0018	
240		0.003	
250		0.005	
260		0.008	
278		0.0178	
280		0.019	
296.3	0.001	0.027	
320.9		M.P.	
487.7	1.0		
767		760	

Romanov (47) and Fabrikant and Kanel (49) found that the characteristics of the cadmium and zinc lamps were similar to mercury arcs but unfortunately they gave no data to show the pressure at which the lamps operated and the efficiencies obtained. The characteristics of the mercury-rare gas discharge tubes were well studied by H. W. Melville(50) using uranyl acetate (52) and monochloracetic acid for absolute calibration. He found an optimum operating condition at a pressure of neon of 5 mm. and a current of 0.186 A. at 186 volts for his lamp. The efficiency in the production of the 2537 Å resonance line was as high as 12%.

Technical details in the construction of a strong and constant source of cadmium resonance radiation cannot be emphasized too much, for it has been due to such mere details that previous workers have not investigated cadmium photosensitized reactions. The main difficulty arises from the fact that cadmium wets the glass of the discharge tube, especially near the leads, and breakage generally results on cooling of the lamp. (40-43).

In the present work two different types of lamps were used: the first entirely separated from the reaction vessel, the second forming a complete unit with the reaction vessel.

Separate Source of Resonance Radiation.

This lamp was built for preliminary investigations of the possibility of obtaining a suitable source and also for a few preliminary investigations on the ethane decomposition and the ethylene hydrogenation. Its shape and size are given in figure III. The use of oxide coated filament electrodes as in the Piranni (44) or as in the Houtermans (33) lamps was considered unnecessary because the whole lamp was designed to be maintained at a temperature of 260°C. The electrodes were hollow iron cylinders welded to nickel wire and to tungsten for the lead through Pyrex. A Corex D tube 7mm. in diameter was sealed to the Pyrex of the electrodes. The transmission of Corex D. no. 970 for 3 mm. thickness is 90% in the region of 3200 Å. Its transmission around 2300 Å is practically zero, and the lower resonance line is thus completely filtered out.

The cadmium was purified and well outgassed by distilling in vacuo, and was placed in the small lateral tube. The breakage caused by the cadmium solidifying or clinging to the walls of the vessel was avoided by using only small quantities of the metal. The lamp was filled to a pressure of 10 mm. with a mixture of neon and helium. The bombarding of the electrodes, filling etc. were done by the usual technique by the Claude Neon Eastern Ltd. The input of the lamp was about 400 volts at 80 M.A. The

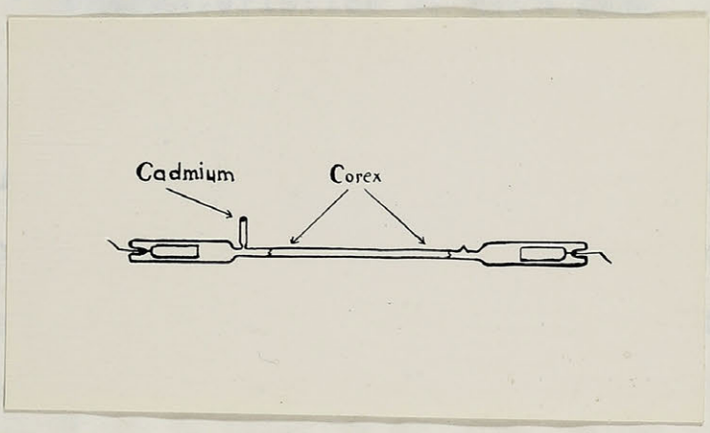


Figure III.

Source of Resonance Radiation (Source A).

total output of ultra-violet was measured with a thermopile after passing through a nickel and cobalt sulphate solution. With corrections for the fraction of λ = 3261 Å absorbed by the filter, the total output was roughly estimated at 7×10^{-7} einstein sec^{-1}.

Characteristics of this Lamp

In general, the steadiness was not very satisfactory. After long runs the lamp would start to flicker. This was due, as further research proved, to the high pressure of the neon gas and to the slow distillation of the cadmium towards the ends of the lamp.

Lamp and Reaction Cell as one Unit.

With the first lamp just described, a cylindrical reaction cell was used. It was placed by the side of the lamp. Due to heavy losses by reflection less than 1/50 th of the light might have been absorbed in the ordinary conditions. It was shown experimentally by Melville and Farkas (53) that the amount of useful radiation in such a case is not proportional to the angle subtended from the lamp by the cylindrical cell because of the large reflection losses from tangential and near tangential surfaces exposed to the light beam. By placing a cylindrical reaction cell close to a

resonance lamp emitting 10^{19} quanta per second, they could utilize only 5 x 10^{16} quanta per second, e.g. approximately 1/200 th of the output. However, in the preliminary investigations, the small cylindrical furnace enclosing the lamp and reaction cell was covered with highly polished aluminum foil, the reflectivity of which is 90% at that wave-length. Thus a fairly large part of the radiation from the lamp was absorbed by the reacting gases.

To still further increase the radiating surface and to minimise the loss due to reflection, a new lamp was built according to the general technique used in neon sign manufacture. The design was similar to that used by Steacie and Phillips (54) for their work on mercury photosensitized reactions. A sketch giving details of construction is shown in figure IV. The emitting part of the lamp consisted of a spiral of 7 mm. internal diameter Corex D tubing. As was said previously, no further filtering was required, Corex D for the thickness employed having a transmission of about 95% at 3261 Å and of virtually zero at 2300 Å. The ends of the Corex spiral were sealed directly to Pyrex tubing of the same diameter. The electrode chambers, also of Pyrex, were 15 mm. in diameter and 7 cms. long. They were inclosing standard neon sign coated electrodes 8 mm. in diameter and 3 cms long. These electrodes were welded through nickel to tungsten wires which were sealed through the glass. A small side tube contained vacuum distilled cadmium.

The Pyrex reaction vessel was sealed on as shown in figure IV. The cell had a diameter of 9 centimeters and a length of 19 centimeters. It contained a sealed-in Corex window 26 mm. in diameter to permit spectroscopic examination of the discharge and also to check the constancy of the output by means of a Weston photoelectric cell provided with a Red Purple Corex filter No 986 transmitting only the resonance line and the weak 3404 Å, 3466 Å, 3613 Å lines. Attention will be given in a further paragraph to the distribution of intensities of these lines and the relative response of the cell.

The whole unit including the electrodes was placed in a furnace (about 20 cms in diameter) which was thermostatically controlled. A thick quartz window was provided on the side of the furnace.

In the first lamp of this type used, the neon pressure at room temperature was 15 mm. This gave a fairly good intensity but trouble soon developed in the form of flickering and unsteadiness of the output. The lamp was therefore refilled with neon at a pressure of 3 mm. The electrodes were replaced by larger "uncoated" nickel electrodes. This gave a much steadier operation, bu still variations as large as 10% were noticed after the lamp had been running for about six hours.

As measurements of the absorption of the resonance line were to be made, a method of obtaining a very

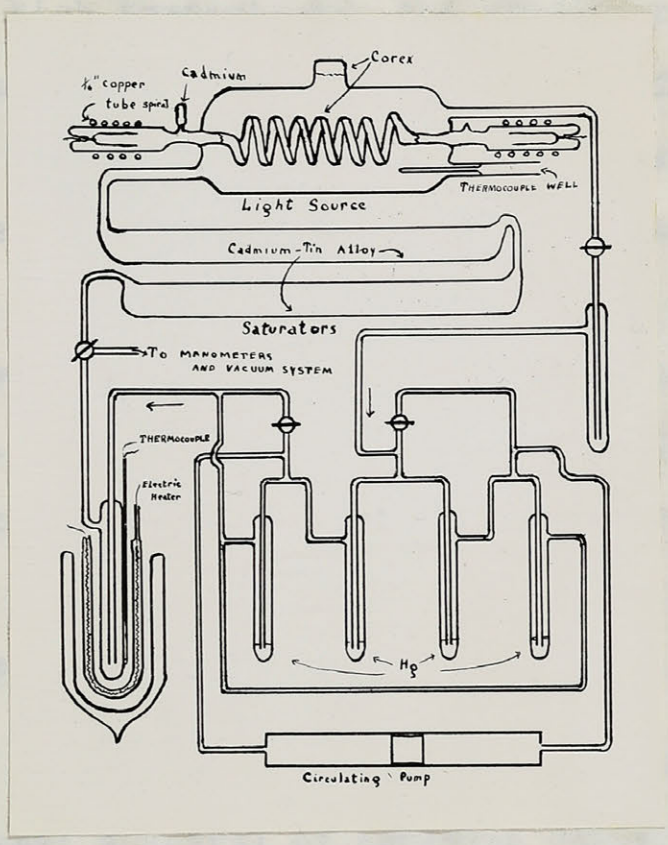


Figure IV.

Source of cadmium resonance radiation, reaction cell and circulatory system.

constant source was sought.

As seen in a previous paragraph, the ideal type of lamp is that of Cario and Lochte-Holtgreven (31) modified by Ladenburg and Zehden (38). In this lamp, only a part is heated to a high temperature, the stationary gas at a pressure of about 3 mm. being circulated by means of a small auxiliary circulating pump, thus preventing any condensation of the metal on the exit window. It is impossible however to use such a lamp satisfactorily in the study of photosensitized reactions owing to the complicated set-up and to the small exit window. It was thought that this could be obviated by using a circulation of the metal vapor instead of that of the foreign gas. A very simple device was employed for this purpose.

Electrode chambers 25 mm. in diameter and 7 cms. long were used; a spiral of annealed copper tube 1/16 th. inch inside bore was fitted on each electrode chamber. A steady stream of air could be circulated independently in each of these spirals. By adjusting this stream, a suitable difference of temperature was maintained between one electrode and the other, thus creating a steady flow of the distilling cadmium vapor. Before each run, the air was circulated through the spiral which had previously been kept hot. In that manner there was always a fresh supply of solid cadmium present in the hotter electrode assuring a sufficient flow of the distilling metal vapor.

This set-up was a great improvement. The lamp took less time to come to a constant output and once attained it was very steady. Measurements with a photocell proved it to be constant within 2% for a period of about 15 hours.

Temperature of the Discharge Tube during Operation.

Great care was taken to check the exact temperature of the lamp spiral (figure IV) under exactly the same conditions as those met with during the experiments on the photosensitized reactions. The lamp was placed in the furnace at 278°C. and was left running for one hour at 110 M.A. and 460 volts. By means of a long thin glass tube, a small thermocouple was introduced into the cell and applied directly to different parts of the discharge spiral tube. A maximum temperature of 294.5°C. was recorded in the middle portion, falling rapidly to 288°C. at the first spiral turn. This small increase of temperature (about 16°C.) is not at all surprising when we consider the high wattage input of the lamp, but it is not large enough to cause any appreciable pyrolysis of the gases under investigation.

The temperature of the furnace was chosen as 280°C. because in the preliminary investigations the lamp had a very good efficiency at that temperature. However, using the set-up just described to obtain a flow of cadmium metal in the discharge tube a good efficiency was noticed at much lower temperatures.

Calibration of the Light Sources.

The intensity of the cadmium resonance radiation was measured in both lamps (figures III and IV).

There are two general ways of measuring the intensity of a light source: by means of a thermopile, and by means of the photochemical action on a well investigated standard (55).

I:- Measurement by means of a Thermopile.

The intensity of the lamp shown in figure III was determined by means of a Moll large surface thermopile connected to a sensitive Leeds and Northup galvanometer. Knowing the total energy falling on a definite surface placed at a known distance from the source, and knowing also the energy of one photon of the resonance line, it was an easy matter to calculate the total emission from the source in quanta per second. A filter of one part pure nickel sulphate and one part pure cobalt sulphate crystals dissolved in five parts of distilled water was interposed in a quartz cell, between the lamp and thermopile. Such a filter is opaque to the visible spectrum but transparent to the ultraviolet below 3300 Å. Since there was some doubt about the transmission of the filter at 3261 Å (only 20-30% is transmitted (56), this method was not very reliable and could give only the order of intensity of the source. This was found to be about

7×10^{-7} einstein per second. For preliminary qualitative work this value was quite sufficient (Light source A).

II Measurements by means of a Standard Photochemical Reaction.

This absolute method of calibration is independent of geometrical optics of the actual system. It is based on the known value of the quantum efficiency of acetone at 300°C. (57). Acetone has been subjected to an extensive study in the gaseous phase. It possesses a broad discrete region of absorption extending from 2200 to 3300 Å with a maximum near 2800 Å. This absorption was studied quantitatively by C.W. Porter and C. Iddings (60) using a spectrographic method. However direct measurements with a photoelectric cell and suitable filters showed this absorption to be, at a temperature of 278°C., a little larger for a wave-lenth of 3261 Å than that obtained from the data of C.W. Porter and C. Iddings at 85°C.

It is to be noticed here that absorption only of the resonance line has to be considered. The first strong line nextto the 3261 Å is the 3404 Å line which is not at all absorbed by acetone.

The quantum yield of the ordinary photochemical reaction of acetone has been well studied at this temperature for quite a number of wave-lengths. It increases from about 0.3 at 60°C. to unity at a temperature of

about 160°C., and from 160°C. to 400°C. no further increase in quantum efficiency is observed (60,65,66). At the temperature of the lamp and cell (278°C.), it was therefore quite reasonable to take the quantum efficiency as unity (66a).

In a general way the decomposition of acetone can be indicated by the following equations:

$$(CH_3)_2CO + h\nu \longrightarrow CH_3 + CH_3CO$$

and

$$2\ CH_3CO \longrightarrow (CH_3CO)_2$$

but at temperatures higher than 60°C. the yield of diacetyl becomes zero (66) and we have:

$$CH_3 + CH_3CO \longrightarrow C_2H_6 + CO$$

Hence the total reaction can be summarized

$$(CH_3)_2CO + h\nu \longrightarrow C_2H_6 + CO$$

Experimental evidence shows this to be correct (64,67). However, at higher temperatures appreciable amounts of methane are formed as shown by Leermakers (66), Patat (68), and Taylor and Rosenblum (81).

In the calibration of the lamp, the rate of decomposition of acetone was therefore inferred from the rate of formation of CO.

The carbon monoxide formed during the reaction was pumped out with a Toepler pumpm the acetone being trapped

first by liquid air and then by acetone and dry ice to set free the CO possibly absorbed by the solid acetone at -180°C. It was then analysed by absorption in a solution of ammoniacal cuprous chloride.

As an illustrative example, data of two runs are given in Table I. For both these experiments, the circulation rate was 1800 cc. per minute, the temperature of the cell 278°C., and the time of illumination one hour.

Table I.

Run No.	Lamp current in M.A.	Voltage	Initial Pressure of Acet.	Final Pressure	Total CO formed	Rate Mole/sec.
1	105	465	92 mm	101 mm	7.4cc	9.3×10^{-8}
2	110	460	92 mm	101 mm	7.6cc	9.5×10^{-8}

For convenience in calculating the absorption, the lamp may be taken to be a point source in the center of the reaction vessel which may be regarded as a sphere of radius R of equal volume to that of the cylindrical cell whose diameter is 2r and length is l

$$R = \sqrt[3]{\tfrac{3}{4} r^2 l} = 6.9 \text{ cm.}$$

A small correction has to be made for the change of absorption during the decomposition of acetone. From the

pressure increase, assuming a decomposition

$$(CH_3)_2CO \longrightarrow C_2H_6 + CO$$

the average pressure of acetone is found to be 85mm. Whence the average absorption during the whole run can be calculated from the equation

$$I_{abs} = I_0 \, \varepsilon \, cd$$

where C is the concentration in moles per liter; d, the thickness in cm; and ε the absorption coefficient. Taking the value of 3.1% as the total absorption, the intensity of this lamp was found to be 3.1×10^{-6} einstein per second(for light source C). Of course, this value is for the source after it had warmed up and attained a constant output.

Accuracy of this Method.

This method of calibration partly rules out the inaccuracy due to the geometry of the reaction vessel, but there enter into the calculation other variables such as the quantum yield, and especially the absorption coefficient of the standard gas employed, the values of which are not too well known in the case of acetone. In fact, since acetone has an absorption range from 3300 Å to 2200 Å with a maximum at 2800 Å, the absorption is rather small at 3261 Å and therefore hard to measure with precision.

If we assume no change in the extinction coefficient with temperature, the data tabulated in the quantitative study of

Porter and Iddings (60) give for a pressure of 85 mm of acetone at 278°C. a percentage absorption of 2.4% using the relation given by Beer's law:

$$\frac{I_t}{I_o} = 10^{-\epsilon cd}$$

However, this assumption is not entirely true. The extinction coefficient may be dependent on the temperature due to the broadening of the line. A direct measurement with a photocell and filter showed the absorption to be equal to 3.1% under the same conditions. Due to the fact that the lamp was of spiral shape and was assumed to be a point source, this value is approximate and should rather be considered as a minimum. It would be a very useful and interesting subject for future work to check the variation of the extinction coefficient of acetone with temperature. It is therefore essential to point out here that due to uncertainties in the absorption of acetone at λ = 3261 Å and to the lack of data on this absorption at high temperatures, this method of calibration is open to criticism, and is only approximate.

Characteristics of the Light Source.

It was found that very little change in the design of the elctrodes, pressure of neon, purity of cadmium, etc. could cause large variations in the total output. A lamp was developed to furnish as much as 5.2×10^{-6} Einstein per

second when operated at 110 M.A. and 460 volts from a Jefferson sign transformer, (the value 3.1% was taken for the absorption). This source, referred to as source B in this work, was used in most of the investigations on photosensitization. However, the less efficient source, referred to as source C, having an output of 3.1×10^{-6} einstein per second was used in all the measurements a) of the variations of the total output with the input wattage, b) of the relative intensities of the resonance line and other lines, c) of the absorption of light by acetone, d) of the absorption of light by a mixture of cadmium vapor and different hydrocarbons.

Variation of Efficiency with the Input.

The efficiency is based here not on the actual total output of the lamp but on the total output which is utilizable. A part of the resonance radiation is absorbed through the Pyrex glass and therefore is not considered in the calculation of the efficiency. Actinometric measurements were used to check a few values in the data given in table II. The rest of these values were obtained by comparison of the light emission employing a sensitive photocell and an appropriate filter. The Red Purple Corex filter used transmitted only the 3261 Å, 3404 Å, 3466 Å and 3613 Å lines. All the other lines were cut out. A preliminary photospectroscopic examination revealed that these secondary lines, relatively weak, varied in a way similar to the resonance line. Thus, it was quite valid to take the value of the light coming through the filter as proportional to the total output of λ=3261 Å.

Table II.

Characteristics of Light Source C.

Current in M.A.	Voltage	Input	Output in Einstein per second	Output in Watt	Efficiency
112	458	52 watts	3.1×10^{-6}	1.15	2.2%
110	460	51	3.0		
105	465	49			
100	475	47	2.9		
95	482		2.8		
90	490	44	2.7	1.0	2.2%
85	495		2.6		
80	500	40	2.5		
75	515		2.4		
70	520	36	2.4		
65	530		2.2		
60	540	32	2.1	0.75	2.3%
55	560		2.0		
50	575	28	1.80	0.67	2.4%

As indicated in table II, it was found that in the region studied the output was fairly well proportional to the input, the efficiency varying from 2.2% to 2.4%.

The highest efficiency attained was with source B (3.8%). This is quite a large value and is comparable to the highest efficiency obtained in mercury discharge tubes; for these Melville (50) has recorded an efficiency of 12% and Phillips 80% (69).

Inert Gas Pressure.

Pressures of 15, 10 and 3 mm. at room temperature were tried in the cadmium discharge tube. Considering the fact that the lamp was run at a temperature of 280°C, 15mm and 10mm. gave unreliable sources. After a long run the light would start to flicker. A 3mm. pressure was considered the optimum pressure securing a more steady and more powerful source.

Distribution of Radiation.

Great care was taken in the determination of the relative intensities of the radiation of different wave-lengths emitted by the cadmium resonance source, since all the following work on absorption depends on the exact value of these intensities. Actually, in the study of absorption, it served a double purpose:

1:- As the absorption of light by gas admixed with cadmium vapour is concerned primarily with the resonance radiation, the other lines in the spectrum not being altered (except the weaker 3404 Å) (20), these other lines were used as a permanent scale for matching the relative intensity of the fading resonance radiation.

2:- The photocell response varies with the wave-length and it was essential to know the exact relative values of the lines which did not vary in intensity and that of the extinguished resonance line for a correct measurement of the absorption by means of the photocell.

Therefore, it is important for the proper comprehension of the following work on absorption to give a detailed description of the study on the relative line intensities in the spectrum emitted by the cadmium lamp.

Light source C was used for this work, cadmium vapour being circulated in the reaction cell as described in a later paragraph. The different spectra were photographed with a small Hilger quartz spectrograph.

In this study an accurate method of photographic photometry was first adopted (70). For a certain wave-length, it may be assumed that there is a definite relation between light intensity and blackening of the emulsion on the photographic plate when all other factors are kept constant. To compare the spectral lines of the same wave-length, it is therefore necessary to have a calibration curve. It has been shown

by Webb (71) that an intermittent exposure is equivalent photographically to a continuous exposure when the rate of flash is so great that each grain of the emulsion receives on the average not more than one quantum per flash. The critical frequency is 10 flashes per second for ordinary purposes: it increases for small quanta. This leads to a convenient method for varying intensity to produce a calibration curve. A rotating disk with variable sectors was therefore used. The disk was rotated at 3600 R.P.M. by a small synchroneous motor giving rise to 120 flashes per second.

However, as it was found that these measurements did not differ with the order of accuracy needed, from those obtained by simply following the Reciprocity law, most of the work was done with this latter method.

The Reciprocity law is based on the approximate statement that the product S of a photochemical reaction is dependent solely on the total energy employed, that is to the product of the factors time t and intensity I.

$$S = It$$

S is measured by the density of the blackening of the plate D which is equal to the logarithm of the opacity.

The wave-lengths involved in the measurement (3261-3404-3466-3613Å) are so near each other in the spectrum that there is no difference of sensitivity in the plate as shown by the spectral sensitivity curves of the plates used (Eastman Process Plate) (74). Hence the Hurter and Driffield

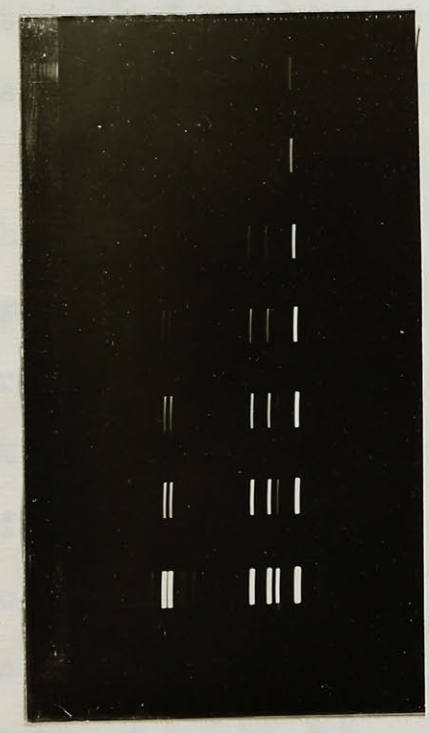
curves (75) will be approximately the same for each of these wave-lengths. The background fog on the plate was reduced to a minimum by using a suitable caustic hydroquinone developer. (76).

A calibration plate is shown in figure V with the different exposure times. The opacities of the lines were measured by means of a microphotometer.

Calibration Plate.

Temperature of lamp: 278°C. Temperature of saturator: 288°C.
Cadmium vapor pressure: 0.018 mm.

4800 Å 3261 Å



Number	Time of exposure.
1	2 seconds
2	4 "
3	8 "
4	16 "
5	32 "
6	64 "
7	420 "

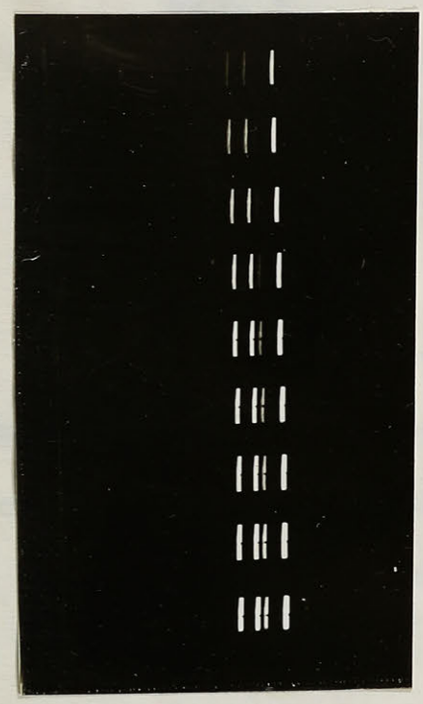
Figure V

The relative intensities of the lines passing through the Corex D exit window were found to be under the experimental conditions:

Line wave-length	Relative intensity.
3261 Å	255
3404	10
3466	48
3613	53
4678	36
4800	35

Mention must be made also of the calibration spectrum of the light passing through a Red Purple Corex A No. 986, Corning Glass filter. The outstanding characteristics of this filter are the large transmission in the region of 3100 Å combined with absorption of most of the visible light of wave-length longer than 4250 Å. It has a second transmission range in the near infra-red, but absorbs the strong 6438.46 Å line of the cadmium. The filter used was 5 mm. thick and was molded, one surface of the unpolished glass being very wavy. It transmitted about 80% of the 3261 Å line. As this filter was used in conjunction with a photocell having a spectral sensitivity varying with the wave-length, it was necessary for accurate work to know the distribution of radiation transmitted. This was accomplished in a way similar to that used in the determination of the relative intensities of the lines in the spectrum.

To show how well the 4678 and 4800 Å lines have been absorbed, a spectrogram is given in figur VI. Experimental conditions are the same as for figure V.



Number	Exposure times.
1	5 seconds
2	10 "
3	15 "
4	20 "
5	40 "
6	50 "
7	60 "
8	100 "
9	120 "

Figure VI

As measured by means of a microphotometer, the relative intensities of the lines transmitted are:

Lines	Relative intensity.
3261 Å	240
3404	10
3466	48
3613	48

The photocell characteristics give the following responses for the wave-lengths considered.

Wave-length	Response of the cell. (approximately)
3261 Å	13%
3404	16
3466	18
3613	23

Thus the response of the photocell to the total resonance radiation emitted through the filter is 60% and 40% for other wave-lengths transmitted. These data were taken as a basis for the calculation of the absorption curves given in a further paragraph.

Saturating Systems.

The hydrocarbons investigated are transparent to the cadmium resonance radiation 3261 Å: the energy transfer occurs by direct absorption of the cadmium resonance radiation by the cadmium vapor giving an excited cadmium atom which in its turn conveys its energy to the reactant gas molecule through a collision of the second kind as shown in the following equations:

$$Cd + h\nu \quad (\lambda = 3261\ \text{Å}) \longrightarrow Cd^* \qquad (1)$$

$$Cd^* + X \longrightarrow Cd + X^* \qquad (2)$$

A sufficient quantity of cadmium vapor must therefore always be present in the reaction cell (a). The process (1) was studied by Terenin (82) and Soleillet (84): they found that only the resonance radiations are excited in cadmium and zinc by the resonance radiations of the same metal. Terenin obtained a good intensity of the resonance lines at a vapor pressure corresponding to a temperature of 150°C. However, to insure a better efficiency of the process (1) a temperature of about 280°C. was used.

Static System.

In the static system used for preliminary investigations, cadmium filings were simply added into the cylindrical Corex reaction vessel. The disadvantage of this system is that cadmium is in large excess in the reaction cell itself and is apt to distill to the walls of the cell thereby reducing its effective transparency.

(a) The ideal conditions for the study of photosensitized reactions would be a very low vapor pressure of the absorbing gas and a weak source possessing a narrow exciting line. Unfortunately, due to other factors, these conditions are not possible in practice. (See fig. II).

Circulatory System.

The circulatory system provides in the reaction cell a continuous flow of the reacting gases admixed with the metal vapor. It thus insures a constant concentration of the cadmium vapor and by interposing traps in the path of the gases it permits the elimination of secondary processes by removing hydrocarbons of higher boiling point from the reaction cell as fast as formed.

The circulatory system employed consisted of a pump made out of a brass tube 36 mm. in diameter and 32 cm. in effective length. It acted as a cylinder in which slid a close-fitting steel piston lubricated with di-butyl phthalate. This piston was driven by an outside moving solenoid. By the proper combination of four mercury valves in the system, it was possible to circulate the gas in one direction only into the reaction cell shown in figure IV. The total displacement of the pump was about 300 cc., so that all the gas could be circulated once about every 8 cycles.

Just before entering the reaction cell the gases were passed into two large saturators providing a surface of more than 70 cm^2 of metal. These saturators were heated in a separate furnace which was thermostatically controlled at 10^oC. higher than the main furnace containing the reaction cell. This insured a good flow of the vapor.

To prevent the Pyrex glass of the saturators from breaking on cooling, an alloy of 50% cadmium-tin fusing at about 200°C. was used (30). The saturators and reaction cell were kept many months at the same temperature thus always maintaining a proper equilibrium of cadmium vapor. It was noticed that a small amount of cadmium distilled into the outside cold tubes near the furnaces forming a small porous plug, which however did not interfere with the circulation. This condensation served as a regulator for the vapor pressure inside the reaction cell preventing it from accumulating on the lamp and exit window. A careful check of the total emission by means of a photocell showed that it stayed constant, proving thereby the constancy of the source and of the transmission.

To have consistent results in the elimination of secondary products at different trapping temperatures, the method already used by Phillips (69) was employed. The trap was immersed in mercury contained inside a double-walled Pyrex glass vessel. A small electric heater was placed between the double wall. When the whole system was plunged in liquid air, the proper temperature could thus be maintained constant for long periods of time by adjusting the flow of current with a variable resistance. The temperature of the trap was measured with a copper-constantan thermocouple placed inside a very thin tube adjacent to the trap. It was calibrated by the B.P. of ethylene at atmospheric pressure, by the sublimation point of carbon dioxide and from -50°C. to 0°C. by means of a standard thermometer.

The main portion of the apparatus comprising the pump, valves, traps, saturators and reaction cell was calibrated with nitrogen. The total volume of the system was found to be 2480 cc. at room temperature, and to hold 1740 cc. of gas at N.T.P. when the saturators were at 288°C. and the cell at 278°C.

This set-up was connected to a manifold leading to the high vacuum system, manometers, McLeod gauge, gas reservoirs, Toepler pump, gas holder, etc.

Materials.

Hydrogen

Hydrogen was purified by passage over platinized asbestos at 600°C. and then through a trap at liquid air temperature.

Ethane.

Ethane was obtained in cylinders from the Ohio Chemical and Manufacturing Company. Analysis showed it to contain from 1 to 2 per cent ethylene, less than 0.3 per cent of hydrogen plus methane, and less than 0.3 per cent of higher hydrocarbons. It was further purified in the following way: It was passed over copper oxide at 300°C., than through saturated bromine water, through a bottle illuminated with a powerful lamp and finally through a 40% solution of potassium hydroxide. After the water had been removed by a trap at -80°C., the gas

was further submitted to a fractional distillation. It was then condensed by means of liquid air into small high pressure cylinders fitted with needle valves. The resulting gas contained no impurities which could be detected with the analytical method used.

Propane and n-Butane.

The propane was also obtained in cylinders from the Ohio Chemical and Manufacturing Company. These gases were stated to be at least 99% pure. They were however submitted to a fractional distillation before using.

Ethylene.

Ethylene was purified only by fractional distillation.

Acetone.

Acetone was reagent grade, obtained from the Eastman Kodak Co. It was submitted to distillation before using.

Cadmium

Cadmium was of C.P. grade, and was purified by distillation.

Method of Analysis.

Analysis of the products was done by the combined use of a fractionating column and of specific absorbents. The heavier

fractions were determined by direct weighing and boiling points.

A semi-micro fractionating column of the Podbielniak type was used (77) for low temperature distillation. It proved to be very satisfactory in the separation of the different hydrocarbons. The main point in the construction of the still was to lessen as much as possible the "dead space". Heavy capillary tubes and stopcocks were used and the spatial distribution of the different reservoirs was also arranged to minimize the dead space thus increasing the accuracy. (See figure VII).

The gases were collected by condensing into a small 10 cc. bulb at the bottom of the still. The rate of reflux was then controlled by varying the quantity of liquid air blown into the head of the column or along the fractionating column itself, and also by varying the rate of warming of the small bulb previously mentioned. The temperature of refluxing was measured at the top by means of a very fine thermocouple placed about $1\frac{1}{2}$ inch below the cooling head.

The distillation of the gas was controlled by an adjustable capillary leak. To have the true boiling points, the pressure in the still were kept at atmospheric during the entire distillation. This pressure was indicated by an auxiliary manometer connected to the still.

Each fraction of gas was measured in a reservoir of known volume. The fractions could then be submitted to combustion to estimate their carbon content.

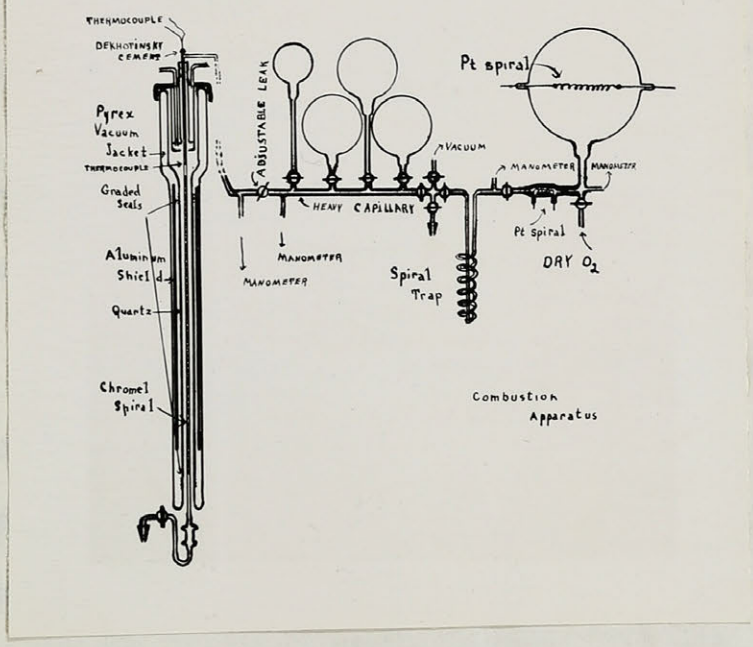


Figure VII

Still and combustion apparatus.

Combustion of the Sample.

A very careful study of the combustion in an ordinary combustion pipette proved that it was incomplete, errors as large as 20% being recorded specially for higher hydrocarbons. A new combustion apparatus, shown in figure VII was built. The combustion bulb contained a large electrically heated platinum spiral in the center and a smaller one placed just near the exit of the gas. By a contraction in the tube, it was arranged so that after combustion in the usual way the gas on being pumped out of the pipette had to pass over this small filament and thus underwent a more complete combustion. A double spiral trap T offering a very large surface permitted a higher pumping speed.

The sample to be analysed was measured in the trap and expanded in the pipette. Oxygen was then run in and the combustion carried out . The combustion products were then slowly pumped off through the trap T immersed in liquid air to retain carbon dioxide and water. The trap was then warmed to room temperature, and the pressure recorded minus the vapor pressure of water at that temperature gave the amount of carbon dioxide formed, after allowing for corrections due to changes in the total volume of the trap and manometer with varying pressure.

With a sufficient quantity of gas, the accuracy was within 1%. In general the cuts were very sharp, indicating a very efficient separation of the different gases. However, it was noticed that ethylene (B.P. -103.8°C.) when present in

small quantities would pass readily with ethane, the separation between these two gases being quite difficult. In the runs following this finding, the fraction containing the ethane was tested for ethylene by means of a Burrell absorbing apparatus, using fuming sulphuric acid as absorbent.

Energy Transfer.

A full knowledge of the degree of energy transfer to the reacting gases is necessary for a correct and intelligent interpretation of the results of a photochemical reaction. In the photochemical and photosensitized reactions this energy transfer will be given by the absorption of light. It may occur by direct absorption by the molecule of the reacting gas as in the ordinary photochemical reaction. This is the case of acetone decomposition, the C=O bond being responsible for the absorption. The energy transfer to the reacting gases may also be the result of a collision with an excited atom (collision of the second kind). This process occurs in two steps which can be schematized as follows in the case of cadmium:

$$Cd(5^1S_0) + h\nu \ (\lambda = 3261\ \text{Å}) \longrightarrow Cd(5^3P_1) \longrightarrow Cd(5^3P_0) \qquad (1)$$

$$Cd(5^3P_1) \text{ or } Cd(5^3P_0) + X \longrightarrow X^* \qquad Cd(5^1S_0) \qquad (2)$$

The efficiency of the absorption of light by step (1) is very great. If no foreign gas is present the energy will be reemitted as light by the inverse reaction:

$$Cd\ (5^3P_1) \longrightarrow h\nu + Cd(5^1S_0)$$

If a foreign gas is present, step (2) occurs to a certain extent. Aside from the number of molecules present, the efficiency of this step will depend mainly on the life of the excited atom, and, also on the ability of the molecule to deactivate. The most efficient deactivators are those possessing a set of vibrations, or a dissociation energy which can take nearly all the energy thus involving a minimum transfer of the excitation energy into kinetic energy. In other words, if a foreign gas molecule has two states differing in energy by the same or nearly the same amount as two electronic states of the activated metal atom, it will have a large quenching effect.

As seen in the Introduction, very little work has been done on the quenching of excited cadmium atoms by gases. Bender (12) found that at 4 mm. the resonance radiation is nearly extinguished by hydrogen. Lipson and Mitchell (13) estimated the half value of quenching at 0.4 mm. for hydrogen and at 60 mm. for methane. No other work is reported on the heavier hydrocarbons.

It was therefore expedient to investigate the light absorption under the exact experimental conditions of the different photosensitized reactions.

Measurements were made first by means of a photocell and filter calibrated as previously described, and then checked by means of spectroscopic photometry. Each measurement was

made as fast as possible to prevent any decomposition. In this method, for sake of simplicity, it was assumed that the 3404 Å line stayed constant throughout. This was shown not to be strictly true by Bender (12), but the assumption introduces a maximum error of the order of only a few per cent.

Acetone Absorption of the Cadmium Resonance Radiation.

Acetone shows a broad discrete band of absorption ranging from 2200 to 3300 Å with a maximum at 2800 Å. The following measurements were made to find to what extent acetone alone absorbs the 3261 Å radiation at a temperature of 278°C.

As the correct value of the intensity of the cadmium resonance radiation source depends on the value of the absorption of the 3261 Å by acetone in the actinometric calibration, a careful measurement of this absorption was made. The reaction vessel and lamp were cleaned with fuming nitric acid and chromic acid to ensure the absence of any trace of cadmium inside the cell. The calibrated photocell and filter were used to investigate the effect. The data given in the following table were taken at a cell temperature of 278°C.

Pressure of acetone in mm.	Per cent of 3261 Å absorbed.
10^{-3}	0
3	0.7 %
10	1.4%
40	2.1 %
90	3.6 %
130	5.8 %

The distance from the lamp, taken as a point source, to the exit window was estimated at 7.5 cm.

Discussion of these results.

Porter and Iddings (60) investigated this absorption thoroughly at a pressure of 75-85 cm. and a temperature of 85° to 100°C. Under these conditions the extinction coefficient was found to be about 0.52 for a wave-length of 3261 Å. Applying Beer's law this would represent an absorption of 2.4 % at a pressure of 85 mm. and a temperature of 278°C., assuming the extinction coefficient to be independent of temperature and the distance from the source to the exit window to be 7.5 cm. However, in the present case the absorption of the resonance line by acetone was found to be 3.1% under the same conditions which would mean an increase in the extinction coefficient with temperature. The accuracy of this determination lies on the assumption that the source may be regarded as a point in the center of the cell, which is only approximate and hence the present results are in agreement with those of Porter and Iddings to within the experimental error.

Absorption of the Cadmium Resonance Radiation by Foreign Gases in the Presence of Cadmium Vapor.

The following data are given for the circulating gases (1800 cc. per minute), the saturators being at 288°C. and the reaction cell at 278°C. corresponding to a cadmium vapor pressure

of 0.018 mm. The distance between the source considered as a point and the exit window was 7.5 cm.

The spectrograms for the absorption of each gas are also given with their respective data. The 3466 Å line for the same time of exposure had the same density throughout and were therefore taken as a standard of comparison. As was seen previously, the relative intensities of the 3466 and of the 3261 Å lines have been found to be in the ratio of about 1::5. Therefore, when the resonance line has the same density as the 3466 Å line, the absorption is 80%. To show that the 3466 Å line is not varying appreciably in intensity by the addition of a gas to the cell, microphotometer readings of the opacity of this line are given in a few cases.

Absorption by Ethane.

a) Photocell measurement.

Pressure of ethane	Percentage absorption.
0.5 mm.	14%
1.0	32
1.5	44
2.0	60
3.0	85
6.0	91
12	93
18	95
30	95
100 mm.	97%

b) Spectroscopic Photometry.

Time of exposure: 40 seconds.

3261 Å

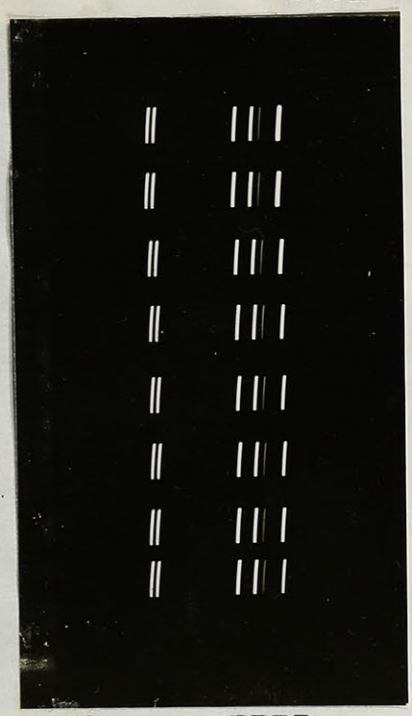


Figure VIII.

Number	Pressure of ethane.
1	0 mm.
2	1.0
3	2.0
4	4
5	8
6	12
7	16
8	40 mm.

The microphotometer gave about 80% absorption at 4mm. of ethane.

Absorption by Hydrogen.

a) Photocell measurement.

Pressure of Hydrogen	Percentage absorption.
0.5 mm.	48%
1.0	61
2.0	71
4.0	78
8	85
16	89
21	97
42	97

b) Spectroscopic Photometry. (30 seconds exposure).

3261 Å

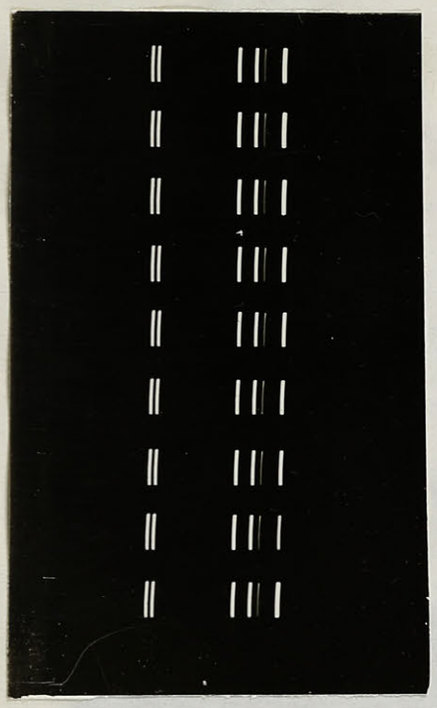


Figure IX.

Number	Pressure of Hydrogen.
1	0.0 mm.
2	0.25
3	0.5
4	1.0
5	2.0
6	4.0
7	8.0
8	25.0
9	0 mm.

The microphotometer gave about 80% absorption at 4.0 mm. of hydrogen.

Absorption by Propane.

a) Photocell measurement.

Pressure of propane.	Percentage absorption.
0.5 mm.	56%
1.0	70
1.5	80
2.0	87
5.0	89
12.0	91

Pressure of propane.	Percentage absorption.
25 mm.	93%
45	97
90	99
160 mm.	99

b) Spectroscopic Photometry.

Time of exposure: 30 seconds.

3261 Å

Number	Pressure of propane.
1	0 mm.
2	1.0
3	3.0
4	8.0
5	16
6	32
7	64
8	128
9	0 mm.

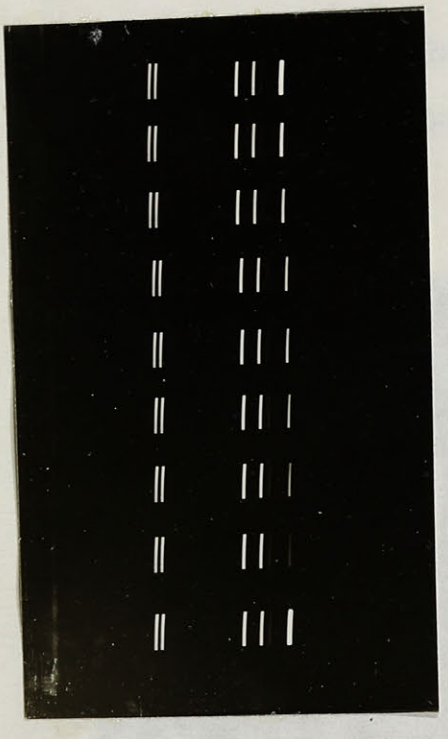


Figure X.

Microphotometer reading: about 80% absorption at 2.5 mm. of propane.

Absorption by Butane.

a) Photocell measurement.

Pressure of butane.	Percentage absorption.
0.3 mm.	63%
1.0	72
1.5	76
4.0	88
9	92
20	92
30	94
50	97
100 mm.	99

b) Spectroscopic Photometry.

Time of exposure: 30 seconds.

3261 Å

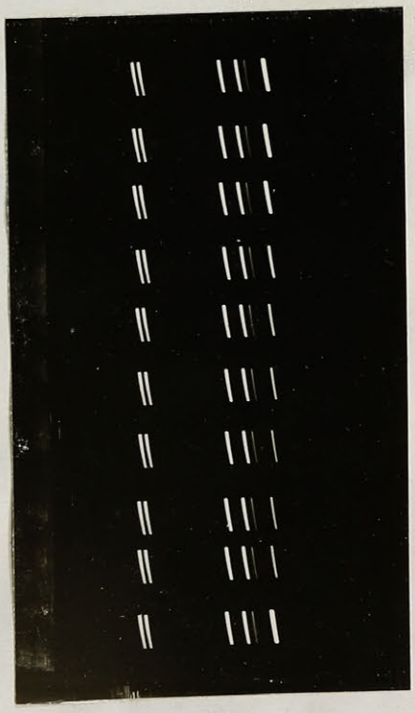


Figure XI.

Number	Pressure of butane.
1	0 mm.
2	1.0
3	2.0
4	4
5	8
6	16
7	32
8	64
9	82
10	0 mm.

The microphotometer gave 80% absorption at about 3 mm. of butane.

Absorption by Ethylene.

Photocell measurement.

Pressure of ethylene.	Percentage absorption.
1.0 mm.	85%
2.0	93
3.0	98
4.0	99
8.0	99
18	99
28	99
42	98
68 mm.	93

Absorption by acetone.

a) Photocell measurement.

Pressure of acetone.	Percentage absorption.
1 mm.	32%
2	48
3	56
4	59
8	61
40	72
92 mm.	56

b) Spectroscopic Photometry.

Time of exposure: 30 seconds.

3466 Å
3613 Å
3261 Å

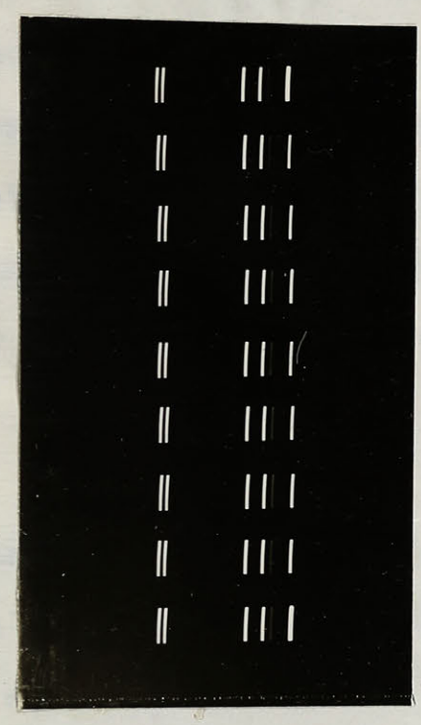


Figure XII.

Number	Pressure of acetone.
1	0 mm.
2	3
3	6
4	12
5	24
6	40
7	60
8	90
9	0 mm.

Microphotometer reading: about 80% absorption at 12 mm. of acetone.

Data showing the constancy of the 3466 Å and 3613 Å lines.

(Figure XII).

Number	Opacity of 3466 Å,	of 3613 Å
1	7.7	7.9
2	7.7	7.9
3	7.7	7.9
4	7.7	7.9

Discussion of the Results on Absorption.

In general, the absorption of the cadmium resonance line by a foreign gas in the presence of cadmium atoms is much more effective than for mercury, its half value being obtained for a pressure of about 0.5 mm. of hydrogen, 0.2 mm. of butane, 0.4 mm. of propane, 1.6 mm. of ethane, and 2.0 mm. of acetone. This is not surprising considering the fact that the excited cadmium atom (5^3P_1) has a mean life about 20 times longer than mercury excited atoms (6^3P_1) (99-101).

Cadmium(5^3P_1): 2.5×10^{-6} second.

Mercury (6^3P_1): 1.08×10^{-7} second.

The chance of a collision between the excited cadmium atom with a foreign gas thus becomes equal to that of the mercury for a much smaller pressure. Furthermore, there is a considerable chance that a Cd(5^3P_1) atom on falling to the (5^3P_0) metastable state will be reverted back to the (5^3P_1) state at the next collision on account of the high kinetic energy of the gas molecule at a temperature of 280°C. and the small energy difference between these two states in the case of cadmium.

It should be noticed also that the data do seem to indicate a more efficient quenching by ethane, propane and butane relative to hydrogen than in the case of mercury. This would mean that the process for example

$$C_2H_6 + Cd(5^3P_1) \longrightarrow C_2H_5 + CdH$$

is highly efficient and comparable in magnitude to the process:

$$Cd(5^3P_1) + H_2 \longrightarrow CdH + H$$

Acetone absorption of the resonance line in presence of excited cadmium atoms is not very efficient. It was observed that this absorption decreased very quickly with exposure indicating the probable formation of an intermediary product which would clean up the cadmium atoms.

It should be emphasized that the above data are by no means equivalent to true quenching efficiencies. They do not obey Stern and Volmer law (16) at least in the higher pressures region, since, under the actual experimental conditions, the ideal resonance lamp is far from being attained. The high concentration of cadmium atoms in the reaction cell would give rise to imprisonment of radiation i.e. reabsorption of the emitted resonance radiation on its way out through the gas to the exit window giving rise to secondary radiation. Even at the lower pressures the Lorentz broadening would alter the results making the Stern and Volmer law inapplicable due to the change of width and position of the absorption line relative to the exciting line.

These absorption values however furnish good information on the actual energy transfer taking place during the cadmium photosensitized reaction. They also give a knowledge of the order of magnitude of the quenching of the

different components in a mixture of gases such as exists after the products of reaction have begun to accumulate.

On the basis of the principle that the deactivation of an excited atom depends on the presence, in the quenching foreign molecule, of a certain degree of resonance with the excited atom, it is clear that there exists a relation between the bond that is ruptured in the primary reaction and the energy supplied by the excited atom, following a collision of the second kind. What is the precise nature of the bond or bonds giving rise to such a degree of resonance in the quenching molecules can be decided by a full knowledge of the primary steps of their photosensitized decomposition.

CADMIUM PHOTOSENSITIZED REACTIONS.

General Procedure.

Static System.

For preliminary investigation of cadmium photosensitized reactions a static system was employed. The experimental arrangement was very simple. The reaction vessel was of Corex (diameter 26 mm.) and had a capacity of 45 cc. It contained cadmium previously outgassed and distilled in vacuo. The lamp was placed at about 5 mm. from the reaction vessel. Both were enclosed in an electric furnace which could be easily removed for cooling down the whole reaction vessel in liquid air. The pressure of the reacting gases could be read on a manometer. The photosensitized reactions were studied at a temperature of 260°C. and at a pressure of about 680 mm. No direct analysis of the products was made , because the purpose of this investigation was only to make sure that the cadmium photosensitized reactions of hydrocarbons had an appreciable speed. This was determined by the total condensable gas in liquid air before and after the exposure. Actually, the small size of the reaction vessel made it possible to immerse it completely in liquid air. The light source A was used.

Circulatory System.

After the preliminary work with the static system, a more complete survey of the reactions was made with the circulatory system. For all these experiments the temperature of the cell was maintained in the region of 280°C. and that of the cadmium saturators at about 285°C. so as to give comparable results.

By a careful study of the absorption, the circulating speed was found to be suitable at 6 cycles of the pump per minute which means a circulation rate of 1800 cc. per minute.

In all runs using light source B, the gases were first measured in a part of the circulatory system (pump and opened valves; Cf. fig. IV). This measured amount was expanded into the reaction cell and saturators when the lamp had come to a constant output. The pressure was immediately read and taken as the initial pressure. The circulation was then started and the gas illuminated for a definite period of time. In these experiments, the trap was left at room temperature, and no attempt was made to remove the products of the reaction during a run.

In runs made with light source C at low trapping temperatures, the amount of gas was measured as previously. In the case of hydrogen-ethane mixtures, a definite amount of hydrogen was introduced first. Ethane contained in a small auxiliary trap cooled in liquid air

was then admitted. In this manner, after necessary corrections for the small volume of the auxiliary trap, the amount of hydrogen and of ethane in the mixture was known accurately. After reading the pressure at room temperature, the trap in the circulatory system was cooled to a given temperature while the circulation was going on. The pressure read when equilibrium was attained was taken as the partial pressure of ethane.

In this last procedure a slight error was introduced in the calculation of the quantum input, since the illumination was started only after the introduction of the reacting gases. There is actually a lag of time before the source gets to its maximum output, once the current turned on. This was measured separately and was found to be approximately as given in the following table for light source C.

Time	Output.
0 minute	0
2	70%
3	95
4	100

A correction based on these data was therefore made.

After illumination, the trap was brought to room temperature and the pressure measured. The gaseous products (with boiling point below room temperature) were then transferred by means of a Toepler pump to a gas holder and finally to the Podbielniak column previously described.

The first fraction containing all the hydrogen and a little methane was analysed in the combustion pipette, and also, the last fraction containing butane and propane. The ethylene content was determined in the fraction containing the ethane.

Higher hydrocarbons which could readily distill at temperature of about 75°C. were distilled in a small trap cooled in liquid air. This trap was provided with a ground joint and stopcock, and its contents could be weighed directly. The vapor pressure of these higher hydrocarbons was also measured.

RESULTS AND INTERPRETATION.

Ethane Decomposition.

In the static system the decomposition of an ethane-hydrogen mixture 12::11 at an initial pressure of 653 mm. and a temperature of 260°C. was as follows:

Pressure	Time of exposure	Temperature of cell
89 mm	o minute	Liquid air
653	0	260°C
646	135	
633	355	
110 mm.		Liquid air.

For a mixture of one part ethane to one part hydrogen, it was:

Pressure	Time of exposure	Temperature of cell
97 mm.		Liquid air
686	0 minute	260°C
673	285	
110 mm.		Liquid air.

The drop of pressure on illumination indicates formation of heavier hydrocarbons. The difference between the portion condensable in liquid air before and after the action of excited cadmium atoms is a proof of the formation of products of lower boiling point than ethane. (Hydrogen and methane).

Ethane Decomposition in the Circulatory System.

Satisfactory results with the static system led to a more general survey of the ethane photosensitized reaction by means of a circulatory system. Ethane alone was first investigated. In the first series of runs no trapping of the heavier products was tried. The results are given in Table III. In this series of experiments light source B was used (5.2×10^{-6} einstein per second). The rate of circulation as in all of the other runs was 1800 cc. per minute. The experimental conditions for all the following runs are the same except for the exposure time which varied from 30 minutes to 360 minutes. The purpose of this procedure was to find what was the main reaction occuring at the first moment of the illumination.

Table III.

The Cadmium Photosensitized Decomposition of Ethane.

(No trapping of the secondary products).

Total volume of system:	2480 cc.
Reaction cell temperature:	278°C.
Saturator temperature:	288°C.
Cadmium vapor pressure in cell:	0.018 mm.
Circulation rate:	1800 cc. per minute.
Resonance radiation:	5.2×10^{-6} einstein per sec.
Lamp current:	110 M.A.
Temperature of trap:	Room temperature.

Table III.

Run No.	Time in minute	Initial pressure	Final pressure	Decomposition rate, moles per sec x 10^6	Quantum Yield
1	30	203 mm.	204	1.6	0.31
2	30	203	204	1.5	0.3
3	30	203	203	1.4	0.29
4	60	203	203	1.4	0.29
5	120	203	205	1.2	0.23
6	180	203	204	1.0	0.19
7	180	203	204	1.1	0.2
8	300	203	204	0.9	0.18
9	360	203	203	0.8	0.15
(10	420	203		0.0	

(Blank run - lamp off.

Table III.

Run No.	Gaseous Products, mole per cent.				Higher Products.
	H_2	CH_4	C_3H_8	C_4H_{10}	
1	51.9	9.1	39.0		
2	49.0	9.0	42.0		Small with low times of exposure, increasing with exposure time.
3	64.1	11.7	24.2		
4	59.0	20.0	21.0		
5	42.5	35.0	16.5	6.0	Mainly hexane.
6	38.0	48.5	7.7	5.8	
7	65.0		32.8	2.2	
8	28.1	66.3	----	5.6	
9	19.2	65.7	4.9	10.2	
10	0.0	0.0	0.0	0.0	----- ----

As will be discussed in detail later, the possible primary reactions of ethane with excited cadmium atoms are:

(1) $C_2H_6 + Cd(5^3P_1 \text{ or } 5^3P_0) \longrightarrow Cd(5^1S_0) + 2\,CH_3$

(2) $C_2H_6 + Cd \quad " \quad " \longrightarrow Cd(5^1S_0) + H + C_2H_5$

or $CdH + C_2H_5$

(3) $C_2H_6 + Cd \quad " \quad " \longrightarrow Cd(5^1S_0) + CH_2 + CH_4$

(1) and (3) would give rise to methane, (2) to hydrogen formation. The actual problem is to know if the hydrogen formed in the reactions is not merely the result of the decomposition of secondary products formed. The solution is found by plotting the ratio of hydrogen to hydrogen plus methane H_2/H_2+CH_4 against time. By the reasonable extrapolation of the curve as shown in Figure XIII, it gives for zero time (first instant of reaction) 100% hydrogen. As it will also be discussed later, this proves that hydrogen atom formation is the <u>only</u> initial step of the cadmium photosensitized ethane decomposition.

It should be remarked that the conditions of study of the cadmium photosensitized ethane decomposition are very favorable on account of a relatively lower efficiency of the reaction investigated by Bender (19)

$$Cd(5^3P_1) + H_2 \longrightarrow CdH + H$$

as compared to that of mercury. In fact, absorption data do seem to indicate a more efficient quenching by ethane,

propane and butane relative to hydrogen than in the case of mercury (Cf. page 68).

In this first series of runs a slight error is introduced due to the fact that as mentioned in the method of analysis a small quantity of ethylene can pass unnoticed in the distillation of ethane. Later on, the content of ethylene was checked for a three hours run and found to be very small (1%).

It was also noticed that after a certain period of illumination the total content of hydrogen remained about the same. Its rate of production is therefore greatly diminished in the later stages of the reaction. To investigate the point further, hydrogen-ethane mixtures were also illuminated under the same conditions. (See Table IV). The main features of these results are the large production of methane, and the fact that hydrogen is still formed, although in much smaller amounts than before, and not consumed as in the analogous decomposition with mercury excited atoms (78). No ethylene is present and the propane formed is much less. In that case, it seems probable that reactions of hydrogen atoms are the main processes since hydrogen appears to be more efficient than ethane in quenching the resonance radiation.

The quantum yield of ethane decomposition in the runs of Tables III and IV is found to vary with the exposure time. This is not at all surprising considering the fact that there is a competition between ethane and the higher

hydrocarbons formed to absorb the incident energy. It should be remembered that at about 1 mm. pressure propane and butane absorb more than 70% of the incident energy. Therefore, after a certain period of illumination the reaction becomes that of the butane and propane decomposition. With the idea of reducing this complication, a series of runs were made at a low trapping temperature (-125°C).

The vapor pressures of butane and propane are quite low at this temperature (about 3 mm. for propane and 0.15 mm for butane). At a pressure of 3 mm. propane when alone absorbs nearly 90% of the incident energy. Since the trapping involves a reduction in the partial pressure of ethane, it increases the chance of reaction of whatever propane and butane remain in the gas phase. Owing also to experimental difficulties in the circulation of the reactant gases, no lower trapping temperature was considered convenient.

Vapor pressure of Propane and Butane.

Temperature	Propane	Butane.
-110°C.	13 mm.	0.7 mm.
-120°C.	5 mm.	0.3 mm.
-130°C.	2 mm.	0.07 mm.

Most of the trapping was done at -125°C. Taking in account the great solubility of butane in liquid ethane, the removal of butane was a little more efficient than can be inferred from the table just given. However, the experiments were considered to be of interest because most of the butane was trapped at -125°C.

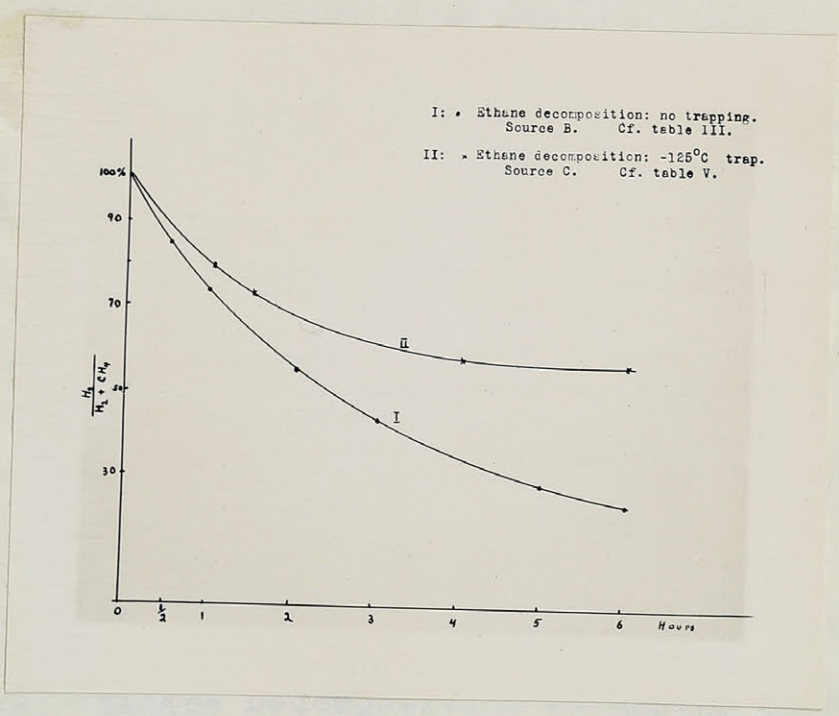

I: • Ethane decomposition: no trapping.
Source B. Cf. table III.
II: × Ethane decomposition: -125°C trap.
Source C. Cf. table V.
100%
90
70
50
30
$\frac{H_2}{H_2 + CH_4}$
0
½
1
2
3
4
5
6
Hours
I
II

Figure XIII.

Data of Figure XIII.

Curve I:- Ethane Decomposition (no trapping of secondary products See Table III).

Run No.	Time	Ratio H_2/ H_2+CH_4
1	30 min.	84.9%
2	30	84.2
3	30	85.1
4	60	74.8
5	120	55.0
6	180	44.1
8	300	29.9
9	360	23.2

Curve II:- Ethane Decomposition (trapping of secondary products) (See Table IV).

Run No.	Time	Ratio H_2/ H_2+CH_4
1	60 min.	78 %
2	90	71
3	240	60
4	360	57.5%

Table IV.

The Decomposition of Ethane-Hydrogen Mixtures.

Operating conditions.

Volume of system:-	2480 cc.
Temperature of reaction cell:-	278°C.
Saturator :-	288°C.
Cadmium vapor pressure:-	0.018 mm.
Circulation rate per minute:-	1800 cc.
Resonance Radiation:-	5.2×10^{-6} einstein per sec
Temperature of Trap:-	Room temperature.
Initial ethane pressure:-	100 mm.
Initial hydrogen pressure:-	100 mm.
Final Pressure:-	200 2 mm.

Table IV.

The Decomposition of Ethane-Hydrogen Mixtures.

Run No.	Time in minute	Decomposition Rate, moles per sec. x 10^6	Quantum Efficiency
1	60	0.8	0.16
2	120	0.7	0.14
3	240	0.7	0.14

The Products of the Decomposition of Ethane-Hydrogen Mixtures.

Run No.	Gaseous Products, mole per cent					Liquid products.
	H_2	CH_4	C_3H_8	C_4H_{10}	C_2H_4	
1	13.2	73.0	13.8	----	---	Quantity increases with time of exposure. Mainly hexane.
2	9.3	70.0	17.2	3.5	---	
3	7.2	75.2	6.9	10.7	---	

Table V.

The Decomposition of Ethane at Low Trapping Temperatures.

Operating conditions.

Temperature of the reaction cell:-	278°C.
Temperature of the saturator:-	288°C.
Cadmium vapor pressure:-	0.018 mm.
Volume of system:-	2480 cc.
Circulation rate per minute:-	1800 cc.
Resonance radiation:-	3.1×10^{-6} einstein per sec.

Run No.	Time in minute	Total vol. of ethane.	Initial pressure	Final pressure	Trap Temperat.
1	60	588	255 mm.	253 mm.	-124°C.
2	90	320	141	139	-115°C.
3	240	324	141	137	-125°C.
4	360	465	202	192	-125°C.

Table V.

The Decomposition of Ethane at Low Trapping Temperatures.

Run No.	Partial pressure of ethane	Fraction of ethane decomposed.	Decomposition rate, moles per sec. x 10^6	Quantum Yield
1	68 mm.	0.23	1.4	0.45
2	150	0.5	1.2	0.39
3	62	0.93	0.94	0.31
4	62	0.96	0.89	0.22

Run No.	Gaseous products, moles per cent.					Liquid products, expressed as weight per cent of total products.
	H_2	CH_4	C_3H_8	C_4H_{10}	C_2H_4	
1	42.4	12.0	40.0	2.6	1.0	5%
2	45.8	18.7	35.5		----	
3	40.9	27.7	23.8	7.0	0.7	13
4	45.5	33.5	11.6	8.9	0.5	20

Table VI.

Cadmium Photosensitized Reaction of Hydrogen-Ethane Mixtures at Low Trapping Temperature.

Operating conditions.

Volume of system	2480 cc.
Temperature of reaction cell:-	278°C.
Temperature of saturator:-	288°C.
Cadmium vapor pressure:-	0.018mm
Resonance radiation:-	3.1×10^{-6} einstein per sec.

Run No.	Time in minute	Total volume	Initial pressures H_2	Initial pressures C_2H_6	Final pressure	Trap Temperature
1	60	465 cc.	101 mm.	101 mm.	198	-125°C.
2	120	461	100	100	205	"
3	180	461	100	100	201	"

Table VI.

The Decomposition of Ethane-Hydrogen Mixtures at Low Trapping Temperatures.

Run No.	Fraction of ethane decomposed	Decomposition rate moles per sec.	Quantum Yield
1	0.52	1.3 x 10^{-6}	0.42
2	0.78	1.1 x 10^{-6}	0.34
3	0.95	0.9 x 10^{-6}	0.29

Run No.	Gaseous Products, mole per cent					Liquid Products expressed as weight per cent of total products.
	H_2	CH_4	C_3H_8	C_4H_{10}	C_2H_4	
1	5.8	60.6	25.4	8.2	----	5
2	26.1	40.8	8.9	24.2	----	10
3	23.2	50.0	10.0	16.8	----	11

Table VII.

The Cadmium Photosensitized Decomposition of Propane.

Operating conditions;

Volume of system	2480 cc.
Trap temperature	25°C.
Resonance radiation	3.1×10^{-6} einstein/sec.
Reaction time	120 min.
Initial pressure	157 mm.
Final pressure	158 mm.
Fraction of propane decomposed	0.40
Quantum efficiency	0.28

Other conditions as in Table III.

Gaseous products, mole per cent.

H_2	6.4
CH_4	67.4
C_2H_4	0.6
C_4H_{10}	25.6

Liquid Products:- 28.1 per cent by weight of the total products.

Composed mainly of C_6H_{14}. Vapor pressure of mixture at saturation at 25°C. 178 mm.

Table VIII.

The Cadmium Photosensitized Decomposition of Butane.

Operating conditions:

Volume of system	2480 cc.
Trap temperature	25°C.
Resonance radiation	3.1×10^{-6} einsteins per sec.
Reaction time	115 minutes.
Initial pressure	202 mm.
Final pressure	202 mm.
Fraction of butane decomposed	0.30
Quantum efficiency	0.29

Other condition as in Table III.

Gaseous products, mole per cent.

H_2	0.6
CH_4	24.2
C_2H_6	28.8
C_3H_8	46.4

Liquid products:- 58.2 per cent by weight of the total products.

Vapor pressure of liquid products:- 210mm.

at 26°C.

Table V gives the results of a series of runs on ethane alone at a low trapping temperature. As estimated from the data of the absorption experiments, it appears that the inhibition of secondary processes was only partially successful. However, since the absorption of incident energy by propane and butane is reduced by the partial elimination of these products, the quantum efficiency of the ethane reaction is higher than in the case of no trapping.

Higher hydrocarbons having a vapor pressure close to that of hexane are present. Due to experimental difficulties, only approximate estimates can be given of the percentage of heavier products. A rough check of the higher hydrocarbons contents could be also inferred from the amount of gas(at room temperature and at atmospheric pressure) left after the run, assuming hexane as the only liquid product. Ethylene is found in small amount.

Curve II, Figure XIII shows the ratio of H_2/ H_2+CH_4 plotted against time. The extrapolation is in good accord with the first series of experiments indicating that hydrogen is the main product at short exposure times. It should be remarked here that the light source C was used in the series of runs represented by curve II, while a stronger light source was used in the one represented by Curve I. This fact explains the difference in the shape and position of these two curves.

The results on the decomposition of ethane in the presence of hydrogen with a trapping temperature of -125°C. are given in Table VI. The quantum yield is approximately 0.4. Hydrogen is still produced and not consumed. Ethylene is not present in detectable amount.

As seen, still lower trapping temperatures for the purpose of lowering the vapor pressure of propane were not feasible with the present experimental conditions. Since the quenching of propane is still very large at the partial pressure corresponding to a trapping temperature of -125°C., it was considered essential to study briefly the decomposition of propane under the influence of excited cadmium atoms. The results are given in table VII, and are of considerable importance. Only a small quantity of hydrogen was found. No ethane is formed in the reaction and ethylene is present in small amount. A heavy product of a little higher vapor pressure than the one found in previous runs on ethane is formed. It would correspond to a mixture of butane and hexane. The quantum yield is about 0.3 .

Butane was also investigated as shown in table VIII. Only a trace of hydrogen is formed, the other products consisting mainly of propane, ethane and methane, and a large proportion of higher hydrocarbons. The quantum yield is about the same as for propane.

It is of interest to note that in the second series of experiments on the ethane decomposition at a low trapping temperature (Tables V andVI), ethylene was present in the

products when ethane alone was exposed to the action of excited cadmium atoms while no ethylene could be detected when a mixture of ethane and hydrogen was illuminated. This naturally suggested hydrogenation of ethylene. Such a reaction had been studied previously in the static system and should be mentioned here.

This preliminary investigation was done with a view of finding the effect of hydrogen concentration on the rate of hydrogenation of ethylene under the action of excited cadmium atoms. The experimental arrangement, as already described, consisted of a Corex reaction vessel (capacity 45 cc.) containing pure cadmium and connected to a manometer. The light source A was placed at 5 mm. from the reaction cell. Both were enclosed in a movable electric oven, the inside of which was covered with polished aluminum foil reflecting as much as 90% (79) of the λ=3261 Å incident light and thus increasing the total absorption by the reacting gases.

Before radiating, the entire vessel was cooled down in liquid air, and the pressure read, and then again after the run another reading was made under the same conditions.

A blank run was first made. No change of pressure was obtained after heating for 17 hours a mixture of hydrogen-ethylene and cadmium vapor at 260° C. showing thereby that no appreciable thermal or catalytic reaction took place at that temperature.

Different mixtures of hydrogen-ethylene in various proportions were exposed to the action of excited cadmium atoms. Curves given in figure XIV and data in Table X show the rate of decrease of the pressure with the time of illumination. In curves I, II, III, the rate decreases rapidly toward the end showing formation of products absorbing a part of the incident energy. With mixtures of high ethylene contents the rate of reaction is nearly proportional to the partial pressure of hydrogen.

The hydrogen taken up in the course of the reaction for a mixture of one part of hydrogen to one part of ethylene is nearly half the total initial amount present. This was shown by the total condensable gases in liquid air before and after the reaction.

The reaction of hydrogen and ethylene was also investigated in the circulatory system. The quantum yield is 0.33 . This value is probably much lower than it should be, the reaction being much faster at the beginning, according to the pressure change. The main factor decreasing the quantum efficiency would be the formation of heavy hydrocarbons absorbing the larger part of the incident energy. The run, the data of which are given in Table IX, was continued until no appreciable change in the pressure was noticed. This however meant that 0.9 of the ethylene had disappeared and secondary products had been formed in large

quantity. The presence of methane in the products is not indicative that it is produced by the direct hydrogenation of ethylene. In fact, Jungers and Taylor failed to find any methane in the mercury photosensitized hydrogenation of ethylene (80). Methane could arise from the secondary decomposition of butane. The large formation of propane and ethane could be accounted for in the same manner. No conclusion on the extent of the secondary reactions can therefore be made until more data are obtained. A systematic investigation of the reaction is intended in the near future using the circulatory system and low trapping temperatures.

The average of two typical runs on the photosensitized study of acetone are given in Table XI. As already mentioned, a strange phenomenon happens when acetone is admitted in the cell with cadmium excited atoms, the absorption first is large enough, but it decreases gradually at a very fast rate. This could possibly be explained by the formation of an intermediary compound which would clean up the cadmium atoms. The quantum yield of the photosensitized reaction was found to be approximately 0.4 on the basis that 70% of the incident resonance radiation is absorbed. In Table XI is also given a complete analysis of the gaseous products. A large quantity of methane is formed along with ethane, carbon monoxide and hydrogen. The high relative contents of methane and hydrogen in the products, as compared to the ordinary photochemical decomposition at the same temperature, could be accounted for satis-

factorily by a subsequent decomposition of the ethane formed in the primary reactions. This secondary decomposition would be favoured by the larger quenching efficiency of ethane.

Table IX.

Cadmium Photosensitized Hydrogenation of Ethylene.

Operating conditions.

No trapping of secondary products.

Cell temperature: 278°C. Cadmium vapor pressure: 0.018 mm.

Time of exposure: 120 minutes

Pressure of hydrogen: 101 mm.)
) Total initial pressure
Pressure of C_2H_4: 101 mm.) 202 mm.

Total volume of mixture: 465 cc.

Circulation rate: 1800 cc. per min.

Final pressure: 102mm.

Fraction of ethylene decomposed: 0.89

Fraction of hydrogen reacting: 0.75

Decomposition rate of ethylene, moles per sec. 1.2×10^{-6}

Quantum yield of ethylene reaction: 0.33

Gaseous Products.

CH_4	32.5%
C_2H_6	33.8
C_3H_8	15.0
C_4H_{10}	18.7

Liquid products present; a part of it is a brown polymer of high B.P.

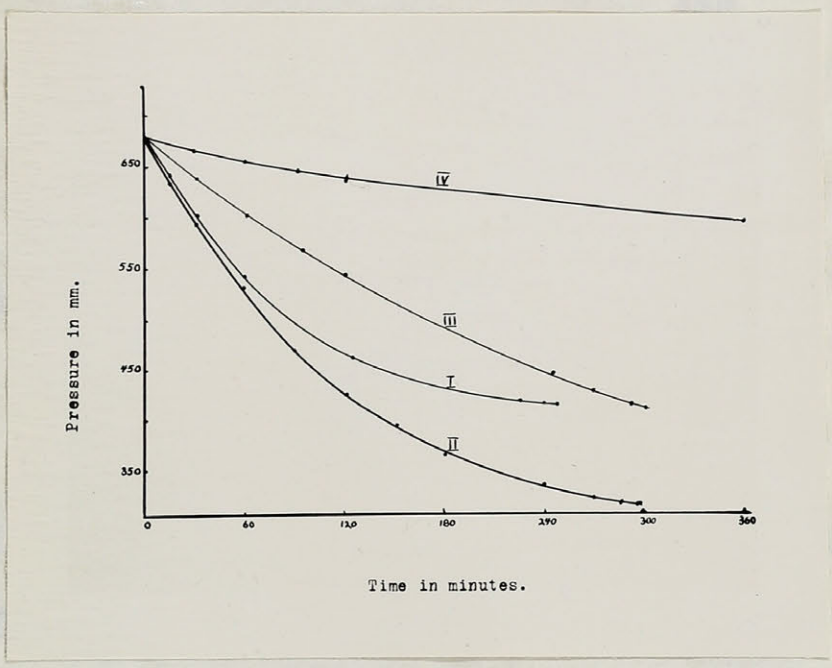


Figure XIV.

Hydrogenation of Ethylene.

Cadmium Photosensitized Reaction of Hydrogen-Ethylene Mixtures.

(Data of Figure XI V)

Curve I: Hydrogen-ethylene 1::1

Pressure	Time	Temperature
98 mm.	0	Liquid air
682	0	260°C.
639	15 min.	
603	30	
540	60	
417	225	
416	245	
415	255	
52 mm.		Liquid air.

Curve II: H_2 - C_2H_4 1::3

Pressure	Time	Temperature.
67 mm.	0	Liquid air.
679	0	
634	15 min.	260°C.
595	30	
485	85	
432	115	
402	135	
361	180	
342	240	
324	270	
322	280	
29 mm.		Liquid air.

Curve III: H_2 - C_2H_4 1::7

Pressure	Time	Temperature
24 mm.		Liquid air
680	0	260°C.
606	60 min.	
571	95	
546	120	
454	240	
428	270	
418	295	
15mm.		Liquid air.

Curve IV: H_2 - C_2H_4 1:::155

Pressure	Time	Temperature
1 mm.		Liquid air
683 mm	0	260°C.
666	45 min.	
662	65	
650	105	
643	120	
567	565	
1 mm.		Liquid air.

Cadmium Photosensitized Decomposition of Acetone.

Operating conditions.

Reaction cell temperature: 276°C.

Cadmium vapor pressure: 0.018 mm.

Circulation rate per min. 1800 cc. per min.

Resonance radiation: 5.2×10^{-6} einsteins per sec.

Initial pressure 92 mm.

Final pressure: (average) 156 mm.

Time of exposure: 60 min.

Fraction of Acetone decomposed: (average) 0.49

CO formed during the decomposition: (average) 112.0 cc.

Decomposition rate: moles per sec x 10^6: 1.4

Average quantum yield on the basis of 70% absorption of incident energy: 0.4

Gaseous Products.

H_2	4.8%
CH_4	40.0
C_2H_6	12.4
Unsaturate:	0.1%
CO:	42.5%

Heavy hydrocarbons: present.

Discussion.

A close consideration of the different possible reactions occuring during the cadmium photosensitized decomposition of ethane in view of discarding the less probable ones will be the modus operandi in this discussion to approach the most probable mechanism.

The primary step in this reaction is the acceptance of the photon energy by the cadmium atom rising it from one electronic state to a higher one. Under the usual experimental conditions, most of the cadmium atoms are at the normal state before their elevation to a higher state by the impinging quanta. Thus only the resonance radiation, according to the transition rules, will be efficient in this process. The only resonance line considered in this work is the $\lambda = 3261$ Å (87 Kcal.), the other one ($\lambda = 2288$ Å) being entirely filtered:

$$Cd(5^1S_0) + h\nu \longrightarrow Cd(5^3P_1).$$

The efficiency of this reaction is beyond doubt (82, 84). Following this step are the possible primary reactions:

Primary Reactions.

(1) $C_2H_6 + Cd(5^3P_1) \longrightarrow C_2H_6 + Cd(5^3P_0)$

(2) " + " $\longrightarrow Cd(^1S_0) + 2\ CH_3$

(3) " + " $\longrightarrow$ " $+ CH_2 + CH_4$

(4) " + " $\longrightarrow$ " $+ C_2H_5 + H$

(4a) $C_2H_6 + Cd(5^3P_1) \longrightarrow CdH + C_2H_5$

(5) $Cd(5^3P_1) + H_2 \longrightarrow CdH + H$

(6) " + " $\longrightarrow H_2^{\ddagger} + Cd$

(7) " + " $\longrightarrow H + H + Cd(^1S_o)$.

Secondary Reactions. (Third body neglected).

A:- Activated Molecule with Molecule.

(8) $H_2^{\ddagger} + C_2H_6 \longrightarrow H + H_2 + C_2H_5$

B: Atom or Radical with Ethane.

(9) $C_2H_6 + H \longrightarrow C_2H_5 + H_2$

(10) " + " $\longrightarrow CH_3 + CH_4$

(11) " + $CH_3 \longrightarrow C_2H_5 + CH_4$

(12) " + " $\longrightarrow C_3H_8 + H$

(13) " + $CH_2 \longrightarrow C_2H_5 + CH_3$ or $C_2H_4 + CH_4$

(14) " + $C_2H_5 \longrightarrow CH_3 + C_3H_8$

(15) " + " $\longrightarrow C_4H_{10} + H$

C: Radical and Atom Recombination.

(16) $H + H \longrightarrow H_2$

(17) $H + CH_3 \longrightarrow CH_4$

(18) $H + C_2H_5 \longrightarrow 2\ CH_3$

(19) H + " $\longrightarrow C_2H_6$

(20) CH_3 + " $\longrightarrow C_3H_8$

(21) $2\ CH_3 \longrightarrow C_2H_6$

(22) $2C_2H_5 \longrightarrow C_4H_{10}$

(25) $2\ C_2H_5 \longrightarrow C_2H_4 + C_2H_6$

D: Other Secondary Reactions .

(23) $H_2 + CH_3 \longrightarrow CH_4 + H$

(24) $C_2H_5 + H_2 \longrightarrow C_2H_6 + H$

(26) $CH_4 + H \longrightarrow CH_3 + H_2$

In the primary reaction, process (1) will be reversible due to the fact that a $Cd(^3P_1)$ atom after releasing some energy and falling to a $(^3P_0)$ metastable state can be reverted back at the next collision, the energy of the gas molecule at 280°C. being of the same magnitude as the small energy difference between these two states in cadmium.

The results from the photosensitized ethane decomposition both at high and low trapping temperatures indicate the formation of hydrogen in the first instant of the reaction. In fact the extrapolation of the curve showing the relation between time of exposure and the ratio $H_2 / H_2 + CH_4$ shows that hydrogen only is formed at the first moment of exposure. (Figure XIV).

If reaction (2) was going in the primary step, the large amount of hydrogen found could never be explained, neither the quick disappearance of the methyl radical formed so as to give the correct ratio of $H_2/H_2 + CH_4$ since this disappearance without formation of methane would be due to the relatively slow reactions (12) and(21). Process (3)

could not likely be explained neither, methane being formed. The only possible step left which would offer an easy explanation of the results is reaction (4) or the more probable reaction (4a), giving rise ultimately to hydrogen atoms. A part of these hydrogen atoms would recombine on the walls (16) in the formation of hydrogen molecules. Hydrogen molecules could also result from the dehydrogenating reaction(9) which would occur at an appreciable rate at 280°C., the activation energy of this reaction being 6.6 Kcal. according to Steacie and Phillips (85) and 11.4 Kcal. according to Trenner, Morikawa and Taylor (83). Reaction (26) would also be appreciable at 280° C.

The disappearance of hydrogen molecules would be accounted for by reaction (5) which was well investigated by Bender (13) and proved to be consistent with the energetically balanced equation on the rough assumption of Svensson (86) of 0.67 volt for the value of the dissociation of normal CdH. Reaction (7) is energetically impossible due to the large energy dissociation of hydrogen compared to that of the excited cadmium atom. Furthermore, the principle of microscopical reversibility would make it very slightly possible. For similar reasons reaction (8) must be rejected as improbable.

Reactions (10), (17), (18), (19), (26) would hinder the formation of hydrogen by using up some atomic hydrogen. To what extent are these reactions occuring? Reaction (10) would be infinitely slow on the basis of the principle of least motion stating that in a primary reaction between a

radical and a molecule there shall be the least change in atomic position and least change in electronic configuration (88). The small probability of reaction (10) has also been shown experimentally by Steacie and Parlee (89). The same conclusion is also postulated in this work to explain propane photosensitized decomposition to account for the absence of ethane in the products.

The activation energy of (17) is small. It would not consume much hydrogen though because it is dependent on the speed of formation of methyl radicals in the secondary steps. Reaction (18) would be highly probable (90). The hydrogen atom recombination with an ethyl radical (19) would reverse the primary process and reduce the quantum yield. Since however, these radicals are at a low concentration, the reaction has a sufficiently low speed.

Considering the high activation energy of reaction (26) its rate must be unappreciable (91). Rice (92) assigns a value of 17 Kcal. to reaction (11) thus making it unlikely. The reactions involving the formation of an hydrogen atom have generally a large activation energy. On that basis reactions (12), (23), (24) can be ruled out.

Since reaction (3) was shown not to proceed, reaction (13) is not occuring. Reaction (14) is probably not very efficient on the basis of the principle of least motion.

The ethyl and methyl radicals would disappear by the different processes (20), (21), (22). The combination of two radicals as in (21) and (22) has been shown to happen at a low rate requiring more than 10 collisions in the case of a methyl radical (93,94,95). Norrish and Appleyard (96) have investigated the addition reaction of methyl and ethyl radicals. They found that it preponderates over any other type of reaction at room temperature. Even at the temperature of the decomposition, the disproportionation reaction

$$2\ C_2H_5 \rightarrow C_2H_4 + C_2H_6$$

would be expected to be small.

The different reactions most likely to occur in the cadmium photosensitized decomposition of ethane may be summarized.(a) It appears certain that the primary step involves a C-H bond split, as in the case of the mercury photosensitized reaction. Since the formation of cadmium hydride has been shown to occur in the presence of hydrogen, it is obviously possible for it to be formed in reaction (4) or (4a). If the reaction occurs by (4) the energy available to split the C-H bond is the excitation energy of the cadmium atom, 87 Kcal., plus a certain amount of kinetic energy. Estimates of the C-H bond strength vary gratly ranging from 92 to 108 Kcal. The values are uncertain, however, and reaction (4) may therefore be possible. Since the heat of formation of CdH from the atoms is 15.3 Kcal., reaction (4a) would be possible provided that the strength of the C-H bond is not much over 102 Kcal.,

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(a) From a paper by Steacie and Potvin, to be published soon.

and (4a) therefore appears to be the most likely primary step. However, in view of the uncertainty in the bond strength, no definite conclusion can be arrived at at present.

Since little methane is formed in the early stages of the reaction, it appears certain that methane formation is not the result of the possible primary step (2). The main possibilities for methane formation are therefore steps (10) and (18). Taylor (15) has discussed the relative probabilities of reactions (10) and (18), and has concluded that reaction (18) probably is of much more importance than (10) as a source of methyl radicals. Recent work of Steacie and Parlee (89) furnishes strong confirmation of this, and it may therefore be concluded that methane formation occurs by (18) followed by (17) and (23). Estimates of the activation energy of the reaction (23) vary, but it should be of some importance at 280°C. It is possible that some methane formation also occurs by (11). This reaction is slow at room temperature, but appreciable at 160°C. (106) and may therefore be important at 280°C.

The higher hydrocarbons presumably result from the recombination of radicals by reactions (20) and (22). The yield of propane is very high in the early stages of the reaction. This differs from the results obtained in mercury photosensitization experiments, where much methane is obtained at all stages and relatively small amounts of propane. This is probably due to the following circumstances. There are three main fates of a methyl radical, viz. combination with a hydrogen atom to form methane, with an ethyl radical

to form propane, or with another methyl radical to regenerate ethane. The third possibility will merely decrease the quantum yield, and will not affect the products of the reaction. At the higher temperatures involved in the present work, reactions (18) and (24) will keep the concentration of hydrogen atoms down to a much lower value. As a result (20) will be much more important than (17), and the production of propane will thus be much greater than in the case of mercury photosensitization experiments at room temperature. In the presence of hydrogen the concentration of hydrogen atoms increases on account of the occurrence of (5), and hence the methane production is higher and that of propane is lower.

The decrease in the relative amount of hydrogen as compared with methane in experiments of long duration is probably partly due to reaction (18). It should be noted, however, that at no stage of the reaction is hydrogen actually consumed. Its rate of formation merely decreases relative to that of methane, and hence its percentage in the products diminishes. This is undoubtedly due to secondary reactions of propane and butane, since as shown by Tables VII and VIII, these decompositions result in a large formation of methane and virtually no hydrogen. In support of this may be cited the fact that in experiments at low trapping temperatures, where the secondary reactions are cut down, the percentage of hydrogen in the products does not diminish appreciably as the run progresses. In these runs the methane increases at the expense of the propane and butane, and liquid products are

formed. It may be noted that the quantum efficiency of the ethane decomposition is higher in experiments at low trapping temperatures, since less of the incident energy is being consumed by secondary processes.

The large production of hydrogen here is also to be contrasted with the results of mercury photosensitization experiments at room temperature, where the stationary hydrogen concentration in a circulating system at low trapping temperatures is very low, and that of methane is high (89). This may be due to relative inefficiency of (5).

The Reaction in the Presence of Hydrogen.

In the presence of hydrogen there is a very large production of methane, and hydrogen is still produced, although in much smaller amount than before. In the presence of hydrogen another primary reaction comes into play (5). In view of the very efficient quenching of cadmium resonance radiation by hydrogen, it is apparent that in a 1::1 hydrogen-ethane mixture the hydrogen is absorbing most of the energy, either by (5) or possibly by (6). Reaction (5) must then be followed by secondary reactions of hydrogen atoms, such as (9). The large yield of methane is evidently due to the increased occurrence of (18) on account of the greatly increased hydrogen atom concentration.

The Decomposition of Propane and Butane.

The main reactions of propane are presumably of the same type as ethane, viz.

$$C_3H_8 + Cd(^3P_1) \longrightarrow C_3H_7 + H + Cd(^1S_0) \quad (27)$$

$$\text{or} \longrightarrow C_3H_7 + CdH$$

$$H + C_3H_7 \longrightarrow C_2H_5 + CH_3 \quad (28)$$

$$C_3H_7 \longrightarrow C_2H_4 + CH_3 \quad (29)$$

$$2\ C_3H_7 \longrightarrow C_6H_{14} \quad (30)$$

The occurrence of reaction (28) appears to be well established by the work of Steacie and Parlee (89) on the reaction of hydrogen atoms, produced by the discharge-tube method, with propane. The propyl radical is known to be unstable at high temperatures, and ethylene formation undoubtedly results from (16). However, preliminary experiments on the cadmium photosensitized hydrogenation of ethylene show that this reaction occurs very rapidly, and hence little ethylene survives in the products.

These results are to be contrasted with recent experiments of Steacie and Dewar (98) on the mercury photo sensitized decomposition of propane. Their results indicate that the reaction is almost exclusively

$$Hg(^3P_1) + C_3H_8 \longrightarrow C_3H_7 + H + Hg(^1S_0) \quad (31)$$

$$2\ C_3H_7 \longrightarrow C_6H_{14} \quad (32)$$

However, their work was done at room temperature, where the propyl radical is stable, whereas here the instability of the propyl radical makes a profound change in the products of the reaction.

The reactions of butane appear to be similar to those of propane.

Summary and Contribution to Knowledge.

I:- An intense source of cadmium resonance radiation has been developed. By the use of a continuous flow of distilling cadmium metal in the discharge tube a steady output is obtained. In addition, self-absorption is minimised.

II:- A new method of absolute calibration for sources emitting between 2800 Å and 3300 Å at temperatures from 160°C. to 300°C. has been applied. The use of acetone as actinometric standard is discussed.

III:- The characteristics of the cadmium resonance radiation source has been studied. The efficiency for $\lambda = 3261$ Å is found to be around 3%. This value increases slightly with decreasing input.

IV:- Absorption measurements of the resonance line in presence of cadmium vapor were made with Hydrogen, Ethane, Propane, Butane and Acetone. It was found that propane and butane absorb more than 50% at pressures of 0.5 and 0.3 mm. respectively.

V:- Cadmium photosensitized reactions of different hydrocarbons were studied in a static system and in a circulatory system with and without trapping of the heavier products. ($\lambda = 3261$ Å).

From these experiments, the following results were obtained:

a) In ethylene-hydrogen mixtures, polymerization of ethylene occurs, and in addition there is considerable hydrogenation. The rate of hydrogenation is nearly proportional to the partial pressure of the hydrogen.

Methane, ethane, propane and butane are formed.

b)An investigation of the cadmium photosensitized decomposition of ethane has been made. The products of the reactions are hydrogen, methane, propane, butane and higher hydrocarbons. It is concluded from the results that the primary process is a C-H bond split, by reaction

$$Cd(5^3P_1) + C_2H_6 \longrightarrow CdH + C_2H_5$$

The secondary steps of importance are the following:

$$CdH \longrightarrow Cd + H$$

$$H + C_2H_5 \longrightarrow 2\,CH_3$$

$$CH_3 + H \longrightarrow CH_4$$

$$CH_3 + H_2 \longrightarrow CH_4 + H$$

$$CH_3 + C_2H_5 \longrightarrow C_3H_8$$

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

From these results, it is concluded that the strength of the C-H bond is not much over 102 Kcal.

The quantum yield of the ethane decomposition is about 0.4 .

c) Propane decomposition has also been studied. Ethane, butane and a small amount of hydrogen are found as gaseous products. The quantum yield is 0.3

By analogy with ethane the following scheme of decomposition is suggested:

$$C_3H_8 + Cd(5^3P_1) \longrightarrow C_3H_7 + CdH$$

$$H + C_3H_7 \longrightarrow C_2H_5 + CH_3$$

$$C_3H_7 \longrightarrow C_2H_4 + CH_3$$

$$2\ C_3H_7 \longrightarrow C_6H_{14}$$

etc.

d) Butane decomposition showed a considerable amount of heavier hydrocarbons in the products. Methane, ethylene and propane were also present. The quantum yield is about 0.3

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