

## The Mechanism of Processes Initiated by Excited Atoms II. Photosensitization by Excited Mercury and Cadmium

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# The Mechanism of Processes Initiated by Excited Atoms

## II. Photosensitization by Excited Mercury and Cadmium\*

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The treatment of the preceding paper is extended to the reactions of excited mercury and cadmium in their triplet and singlet states. It is shown that with the hydrogen molecule quenching of a physical nature is prohibited for the triplet atoms by the necessity for conservation of spin angular momentum, and that dissociation must take place with the initial formation of the metal hydrides. In the reactions of Hg  $^3P_0$ , Cd  $^3P_1$ , and Cd  $^3P_0$  these are also final products, but with Hg  $^3P_1$  and the singlet excited atoms, dissociation of the hydride into the metal and a hydrogen atom takes place at once. Quenching to the metastable state is found to be usually inefficient. The atoms react with saturated hydrocarbons by splitting off a hydrogen atom, but the unsaturated ones usually interact with the initial formation of an excited molecule which when activated by singlet atoms have vibrational energy only, but which with triplet atoms are excited to triplet electronic states. The subsequent reactions of the excited olefines are discussed with reference to the experimental material.

### INTRODUCTION

OF recent years a considerable amount of work has been done on the reactions of excited mercury and cadmium.<sup>1</sup> Mercury possesses important resonance lines at 2537Å and 1849Å, but most of the experimental work has been done with the former, which corresponds to the transition  $6^1S_0-6^3P_1$ . The amount of energy liberated when a triplet mercury atom passes into its lowest state is 112.2 kcal. per mole, which is sufficient to cause dissociation of many molecules, particularly as a further amount (8.5 kcal. per mole in the case of hydrogen) of energy may be liberated simultaneously if the quenched atom combines with one of the products of the

dissociation. The corresponding energy for triplet excited cadmium is somewhat less, 87.3 kcal. per mole, but this again may be increased, by 15.5 kcal., if cadmium hydride is formed. The energies liberated by the four excited atoms are summarized in Table I.

Quenching experiments have so far only been carried out with mercury<sup>2</sup> and cadmium<sup>3</sup> in their triplet states. The data are given in Table I of Part I (preceding paper). The chemical reactions which are initiated by the excited atoms have been studied, using the usual kinetic methods, with mercury and cadmium in both the triplet and singlet states, although the majority are with the triplet atoms. Most of the work has been with hydrogen and the hydrocarbons.

In the remainder of this paper the treatment of Part I is extended to the simpler primary reactions occurring between excited mercury and cadmium atoms and other substances.

TABLE I.

Metal	Line A	Transition	Energy of excited atom kcal.	Total available energy if hydride is formed kcal.
Mercury	2537	$6^1S_0-6^3P_1$	112.2	120.7
Cadmium	3261	$5^1S_0-5^3P_1$	87.3	102.8
Mercury	1849	$6^1S_0-6^1P_1$	153.9	162.4
Cadmium	2288	$5^1S_0-5^1P_1$	124.4	139.9

\* Contribution No. 1031 from the National Research Laboratories, Ottawa, Canada.

<sup>1</sup> For reviews, see E. W. R. Steacie, *Ann. N. Y. Acad. Sci.* **41**, 187 (1941); W. A. Noyes and P. A. Leighton, *Photochemistry of Gases* (Reinhold Publishing Corporation, 1941), Chapter V.

<sup>2</sup> H. A. Stuart, *Zeits. f. Physik* **32**, 262 (1925); W. A. Noyes, *J. Am. Chem. Soc.* **49**, 3100 (1927); A. C. G. Mitchell, *Zeits. f. Physik* **49**, 228 (1928); J. R. Bates, *Proc. Nat. Acad. Sci.* **14**, 849 (1928); *J. Am. Chem. Soc.* **52**, 3825 (1930); *ibid.* **54**, 569 (1932); M. W. Zemansky, *Phys. Rev.* **36**, 919 (1930); M. G. Evans, *J. Chem. Phys.* **2**, 445 (1934); E. W. R. Steacie, *Can. J. Research* **B18**, 44 (1940).

<sup>3</sup> H. C. Lipson and A. C. G. Mitchell, *Phys. Rev.* **48**, 625 (1935).

## REACTIONS OF TRIPLET EXCITED MERCURY

## Reaction with Hydrogen

The potential-energy surfaces for the reaction  $\text{Hg}(^3P_1) + \text{H}_2(^1\Sigma^+_g)$  are shown in Fig. 1, the curves on the left-hand face of the cube being those for an infinite H—H separation, those on the right for an infinite Hg—H separation. The reaction  $\text{Hg}(^3P_1) + \text{H}$  may first be discussed in terms of the former curves.

The curves for the homopolar states may be constructed from the spectroscopic data;<sup>4</sup> it should be noted that there is no repulsive state which dissociates into normal Hg and H. An  $\text{Hg}^+(^2S)$  ion interacts with an  $\text{H}^-(^1S)$  ion with the formation of a polar  $^2\Sigma^+$  state, but the corresponding curve cannot be constructed owing to lack of information from crystal data; however, neglecting the exchange interactions it is found that the polar curve cuts the  $^2\Pi$  curve, the lowest formed from  $\text{Hg}(^3P_1)$  and  $\text{H}(^1\Sigma^+)$ , at a separation of about 3Å. Since the curve for the polar state does not cut that for the lowest ( $^2\Sigma^+$ ) state of the  $\text{HgH}$  molecule, which is known to be the case from the fact that the lowest state is homopolar, and since there is no other (repulsive) state, it is clear that quenching by the hydrogen atom can only arise from a jump from the polar to the  $^2\Sigma^+$  state; as these are probably well separated the quenching efficiency is low.

The surfaces connecting the two sets of curves in the interior of the figure may now be discussed. If a hydrogen atom ( $^3S$ ) approaches linearly an  $\text{HgH}$  molecule in its lowest state

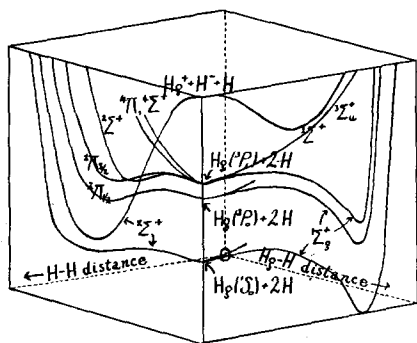


FIG. 1. Potential-energy surfaces for the linear system  $\text{Hg}-\text{H}-\text{H}$ . The curves arising from the  $^3P_2$  state of mercury are omitted for simplicity, and some of the repulsive curves are only continued a short distance.

<sup>4</sup> Cf. R. S. Mulliken, Rev. Mod. Phys. 4, 1 (1932).

( $^2\Sigma^+$ ) the resulting states are  $^1\Sigma^+$  and  $^3\Sigma^+$ , and of these, on account of the relationships

$$\text{Hg}(^1S) + \text{H}_2(^1\Sigma^+_g) = \text{HgH}_2(^1\Sigma^+) \quad (1)$$

$$\text{and } \text{Hg}(^1S) + \text{H}_2(^3\Sigma^+_u) = \text{HgH}_2(^3\Sigma^+), \quad (2)$$

the  $^1\Sigma^+$  state arises from the attractive state of hydrogen and the  $^3\Sigma^+$  from the repulsive. The curves for  $\text{HgH}(^2\Sigma^+)$  and  $\text{H}_2(^1\Sigma^+_g)$  are therefore connected by a  $^1\Sigma^+$  surface which has the same general form as the lowest surface in the  $\text{Na} + \text{H}_2$  reaction. A second,  $^3\Sigma^+$ , surface connects the curves for  $\text{HgH}(^2\Sigma^+)$  and  $\text{H}_2(^3\Sigma^+_u)$ ; this is a highly repulsive surface, its lowest point being the lowest point on the curve for  $\text{HgH}(^2\Sigma^+)$  when the second hydrogen atom is at infinity.

The lowest state of  $\text{HgH}$  which arises from  $\text{Hg}(^3P_1)$  and a normal hydrogen atom is  $^2\Pi$ , and this interacts with a second hydrogen atom to give  $^3\Pi$  and  $^1\Pi$  states. In view of the further relationships

$$\text{Hg}(^3P_1) + \text{H}_2(^1\Sigma^+_g) = \text{HgH}_2(^3\Pi, ^3\Sigma^+) \quad (3)$$

and

$$\begin{aligned} \text{Hg}(^3P_1) + \text{H}_2(^3\Sigma^+_u) \\ = \text{HgH}_2(^3\Pi, ^3\Pi, ^5\Sigma^+, ^3\Sigma^+, ^1\Sigma^+) \end{aligned} \quad (4)$$

the  $^3\Pi$  surface is clearly the lowest, and the only one of immediate interest. For the triangular configuration it may be assumed that the corresponding state is slightly attractive.

There are two comparatively low-lying surfaces representing ionic states of the  $\text{HgH}_2$  complex. The lowest ionic state of the  $\text{H}_2^-$  molecule is  $^2\Sigma^+$ , and this interacts with a normal ( $^2S$ )  $\text{Hg}^+$  ion to give  $^3\Sigma^+$  and  $^1\Sigma^+$  states; similarly the lowest ionic state of  $\text{HgH}$  ( $^2\Sigma^+$ ) interacts with a  $^2S$  hydrogen atom to give  $^3\Sigma^+$  and  $^1\Sigma^+$  states. Two surfaces therefore connect the  $\text{Hg}^+\text{H}-(^2\Sigma^+)$  and  $\text{H}_2^-(^2\Sigma^+)$  curves in Fig. 1, of which that for the  $^1\Sigma^+$  is lower and corresponds roughly to the electron being on the hydrogen atom nearer to the mercury atom; the  $^3\Sigma^+$  state corresponds to the electron being on the farther atom. In the isosceles-triangular configuration the polar states have no such simple significance.

The potential-energy profiles drawn parallel to the Hg—H axis for the linear configuration, and corresponding to the normal H—H separation in hydrogen, are shown schematically in Fig. 2, in which only states corresponding to

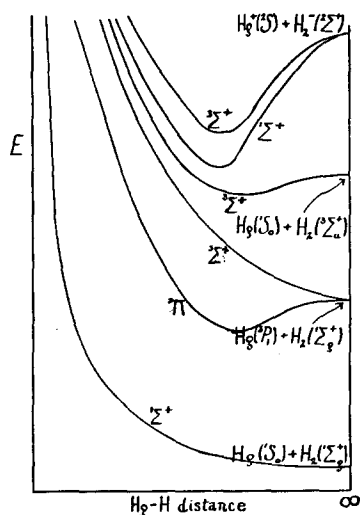


FIG. 2. Potential-energy profiles for  $\text{HgH}_2$  in the plane corresponding to the normal  $\text{H}-\text{H}$  distance.

excited mercury in the  $^3P_1$  state are shown. It is seen that owing to the high energy of the  $\text{H}_2^-$  ion at this  $\text{H}-\text{H}$  separation the polar curves do not cut the homopolar ones; extension of the bond must therefore take place for reaction to occur in some section such as that shown in Fig. 3. As in the case of the quenching of sodium the activated state may be either at the top of the rotational-energy barrier, or at a point where the homopolar  $^3\Pi$  surface is cut by the polar  $^3\Sigma^+$  one, there being a restriction to crossing to the  $^1\Sigma^+$  polar surface owing to the change of multiplicity. In either case there is a statistical factor of  $\frac{1}{2}$  in the rate expression due to the fact that the  $\text{Hg}^+$  and  $\text{H}_2^-$  may approach one another initially either on the  $^3\Sigma^+$  or the  $^3\Pi$  surface of which only the latter leads to rapid reaction. The theoretical value of  $r_{\ddagger}$  must therefore be divided by  $\sqrt{2}$  to be directly comparable with  $\sigma$ . The value of  $\sigma$  is about 2.5Å (Table I, Part I) so that  $r_{\ddagger}$  should be about 3.5Å. This distance is a reasonable one for a crossing point but rather smaller than the value at the top of the rotational-energy barrier (4–5Å). Agreement in the latter case could, however, be given by a value of  $\kappa$  of less than one-half.

The mechanism by which the reaction proceeds to the final state may now be discussed, and this will be done in terms of the linear configuration of atoms. It has been seen that the polar surface on which the system finds itself is

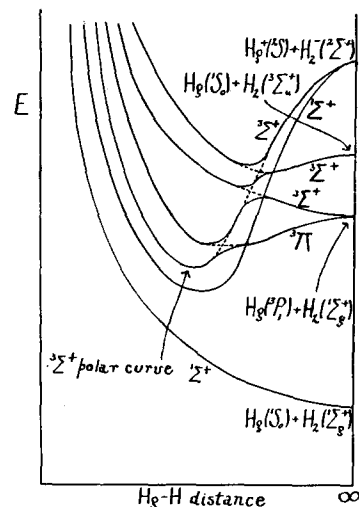


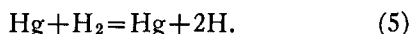
FIG. 3. Potential-energy profiles for  $\text{HgH}_2$  corresponding to an extension of the  $\text{H}-\text{H}$  bond. Reaction initially proceeds along the  $^3\Pi$  homopolar surface, followed by a crossing to the  $^3\Sigma^+$  polar surface. The transition to the  $^3\Sigma^+$  repulsive surface takes place after an even greater extension of the  $\text{H}-\text{H}$  bond has taken place.

for a  $^3\Sigma^+$  state, so that a transition to the lowest,  $^1\Sigma^+$ , state can only take place with difficulty owing to the change of multiplicity. Reaction therefore occurs more readily by a transition from the  $^3\Sigma^+$  polar surface to the  $^3\Sigma^+$  repulsive homopolar surface connecting the  $\text{HgH}(^2\Sigma^+)$  and  $\text{H}_2(^3\Sigma^+)$  curves. At large  $\text{H}-\text{H}$  separations, which may readily take place on the polar surface, this transition may be effected at a point below that corresponding to the first crossing point. The subsequent path of the system corresponds to its finding its way to the lowest part of this repulsive,  $^3\Sigma^+$ , surface, that is to that part which corresponds to  $\text{HgH}(^2\Sigma^+)$  and  $\text{H}(^2S)$ . The quenching of excited mercury by hydrogen is therefore of a chemical rather than a physical nature, the  $\text{H}-\text{H}$  bond being broken.<sup>5</sup>

The exact mechanism by which the process takes place is, of course, extremely complex and could not, at the present stage, be treated theoretically. One can be fairly certain, however, that a large fraction of the energy set free, 17.7 kcal., passes into vibrational energy of the  $\text{HgH}$  molecule, the dissociation energy of which is 8.5 kcal. per mole; the alternative suggestion that it becomes relative translational energy implies

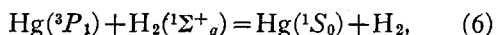
<sup>5</sup> G. Cario and J. Franck, *Zeits. f. Physik* **11**, 161 (1922).

that the mass point proceeds along the lowest point of the valley, which would seem improbable in view of the complicated form of the surfaces. The HgH molecule will therefore decompose within the period of one vibration, so that the over-all reaction is indistinguishable from<sup>6</sup>



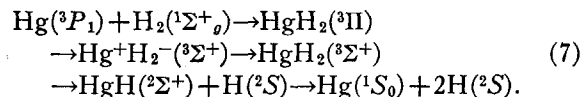
This conclusion is in accord with the findings of Olsen,<sup>7</sup> who showed spectroscopically that HgH is not produced in the reaction in the normal state, but only excited, presumably by secondary reactions. It is interesting to note that in the case of the reaction between hydrogen and mercury in the metastable (<sup>3</sup>P<sub>0</sub>) state the energy available for transfer into vibrational energy, 12.7 kcal., may not be converted efficiently enough into vibrational energy to permit dissociation of the HgH molecule; it might, therefore, be possible to detect HgH in its normal state in a system in which this reaction is occurring.

In view of the application of these principles that is made below to the reactions of the hydrocarbons, the mechanism of the reaction of hydrogen may be considered from a slightly different point of view. The "physical" type of reaction,



analogous to that which takes place with sodium, is here restricted by the necessity for conservation of spin angular momentum (the "Wigner spin conservation rule") unless the hydrogen on the right-hand side is in a triplet state; if this condition is satisfied, however, the molecule at once dissociates, so that the reaction is not of a physical nature. There is therefore little possibility of the hydrogen molecule taking up the excitation energy in the form of vibrational, rotational or relative translational energy, as it was able to do with excited sodium; reaction can only proceed effectively by a dissociation of the hydrogen. The detailed examination which has been made of the mechanism shows the most

probable reaction path to be



It is to be particularly noted that the over-all change has taken place without there being, at any stage, a restriction due to change of multiplicity, compensating changes in the hydrogen molecule taking place to preserve spin angular momentum. It will be seen in dealing with the reactions of hydrocarbons that arguments of this kind are frequently extremely useful in excluding mechanisms which might otherwise be considered. It may be mentioned that the selection rules imposed upon these molecular systems by the necessity of conserving spin angular momentum are obeyed almost rigorously.

### Quenching to the Metastable State

Apart from quenching by hydrogen, oxygen and the hydrocarbons, the other gases given in Table I of Part I quench by transferring the excited mercury atom to the metastable state; this is known to be true as the presence of the metastable atoms can be demonstrated spectroscopically. A potential-energy profile for quenching by a molecule M to the metastable state, which lies 5.03 kcal. below the <sup>6</sup>3P<sub>1</sub> state, is shown in Fig. 4. The system first finds itself in the dip of the middle curve. If M is an atom the quenching process is clearly inefficient, but otherwise the dip is a section through a de-

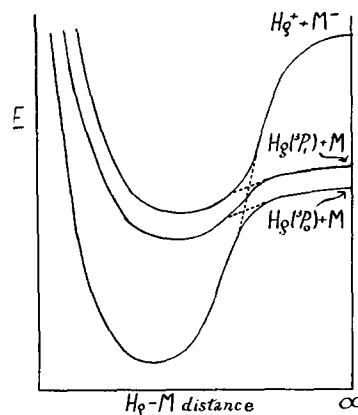


FIG. 4. Potential-energy curves for the quenching of Hg(<sup>3</sup>P<sub>1</sub>) to the metastable state by an atom or molecule M.

<sup>6</sup> Cf. J. Franck and H. Sponer, *Nachrichten Göttingen* 241 (1928); H. Beutler and E. Rabinowitch, *Zeits. f. physik. Chemie* B8, 403 (1930).

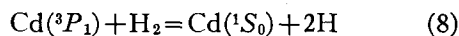
<sup>7</sup> L. O. Olsen, *J. Chem. Phys.* 6, 307 (1938).

pression in three or more dimensional space, and owing to the possibility of a redistribution of energy the complex will not necessarily redissociate into  $\text{Hg}(^3P_1) + \text{M}$ , but may perform a series of vibrations until a transition to the lower surface is possible. The efficiency of quenching to the metastable state is lower than generally obtains for quenching to the normal state since, owing to the small difference between the energies of the  $^3P_1$  and  $^3P_0$  levels, the rate with which the complex redissociates into  $\text{Hg}(^3P_1)$  and  $\text{M}$  is by no means negligible. The apparent quenching efficiency is also lowered in reactions of this kind by the fact that  $^3P_0$  mercury atoms may become excited to the  $^3P_1$  state by collisions.

Zemansky<sup>8</sup> has attempted to show a relationship between the efficiency of quenching to the metastable state and the nearness of a vibrational level of the quencher to 5.03 kcal., the energy of the transition  $^3P_1 \rightarrow ^3P_0$ . The hydrocarbons must, however, be removed from his figure as they are now known to quench by a chemical mechanism (see below), and when they are removed the existence of the relationship can hardly be maintained. In any case it is doubtful whether such a connection has any theoretical justification, as the restriction to crossing caused by a failure of levels to fit is probably usually only slight.<sup>9</sup> It would appear from the present treatment that the problem requires a detailed construction of the potential-energy surfaces relevant to each individual case, and a calculation from them of the course of reaction. This could hardly be attempted at the present stage.

#### REACTIONS OF TRIPLET EXCITED CADMIUM

The potential-energy surfaces for the quenching of the cadmium 3261 line by hydrogen are similar in general form to those for the mercury reaction shown in Fig. 1. The chief difference arises from the fact that, owing to only 87.3 kcal. of energy being liberated in the transition  $\text{Cd}(^3P_1) \rightarrow ^1S_0$ , the process



is endothermic to the extent of 15.6 kcal., and

therefore slow since the activation energy is at least this amount. The reaction which forms  $\text{CdH}$ ,



is much faster since it is only endothermic by c. 0.1 kcal. The quenching reaction is therefore largely reaction (9), which has a slight activation energy of at least 0.1 kcal. This activation energy accounts for the lower value of  $\sigma$  as compared with the mercury reaction (see Table I, Part I).

The chief difference between the mechanism of the quenching of cadmium and that of mercury is that in the former case very little energy can pass into vibrational energy of the hydride, any that does so having to be paid for as activation energy. The hydride  $\text{CdH}$  will therefore not dissociate and should be detectable in its normal state; this has been done spectroscopically by Bender.<sup>10</sup>

The quenching of cadmium atoms in the metastable state will also proceed by a mechanism analogous to (9), but the activation energy will be increased by 1.5 kcal., the difference between the  $^3P_1$  and  $^3P_0$  levels, and the process is consequently inefficient; this, however, has not been investigated, as the levels are separated so slightly as to be difficult to distinguish experimentally.

Owing to the comparative slowness of the quenching by this mechanism, complications may arise in the form of quenching of other types; thus the quenching may be partly due to a physical type of reaction which took place in the quenching of sodium by hydrogen, although as was seen for mercury such a reaction is restricted by a difference in multiplicity between the polar and the final state. A certain amount of the quenching may also be quenching to the metastable state, although this, as has been seen, is inefficient. In any case a considerable fraction of the total reaction must proceed by the chemical process since hydrogen atoms are known to be formed in quantity.

Apart from the hydrocarbons most of the other quenching reactions proceed by transferring the cadmium atom to the metastable state, and, as this lies only 1.5 kcal. below the

<sup>8</sup> M. W. Zemansky, *Phys. Rev.* **36**, 1919 (1930).

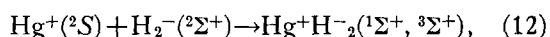
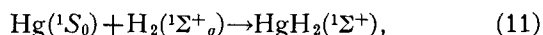
<sup>9</sup> Cf. J. L. Magee, W. Shand and H. Eyring, *J. Am. Chem. Soc.* **63**, 677 (1941).

<sup>10</sup> P. Bender, *Phys. Rev.* **36**, 1535 (1930); cf. L. O. Olsen, reference 7.

$^3P_1$  state, quenching is inefficient owing to the high probability of the system returning to its initial state (cf. Table I, Part I).

#### REACTIONS OF THE SINGLET EXCITED ATOMS

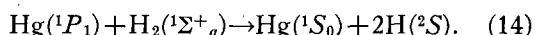
Owing to the non-existence of quenching data and the scantiness of the kinetic information, the reactions of singlet ( $^1P_1$ ) excited mercury and cadmium will only be treated briefly; surfaces may, however, readily be constructed if needed. The term relationships required are, for mercury:



and



with identical states for the cadmium system. The possibility of physical quenching, without dissociation of the hydrogen, may first be considered. It is seen that this may occur *via* the two  $^1\Sigma^+$  states of  $\text{HgH}_2$  and the  $^1\Sigma^+$  state of  $\text{Hg}^+\text{H}_2^-$ ; reaction (10) first takes place to give  $\text{HgH}_2(^1\Sigma^+)$ , followed by a crossing to the  $^1\Sigma^+$  polar state and a second crossing to the lower  $^1\Sigma^+$  state of  $\text{HgH}_2$ , which then dissociates into  $\text{Hg}(^1S)$  and  $\text{H}_2(^1\Sigma^+_g)$  by the reverse of reaction (11). However in both the mercury and cadmium reactions the hydrogen so produced would probably have sufficient vibrational energy for dissociation to take place at once, so that the overall reaction will be



Alternatively, the reaction may be envisaged as taking place *via*  $\text{HgH}(^2\Sigma^+)$  and  $\text{H}(^2S)$ , which may arise from the lower  $^1\Sigma^+$  state of  $\text{HgH}_2$  (reverse of reaction (13)); however the  $\text{HgH}$  will probably have sufficient energy to dissociate. There thus seems to be no alternative to assuming that reaction (14) is the one which takes place.

The quenching cross sections for the atoms in the singlet states should be higher than those for the triplet states, since the surfaces upon which the reaction initially moves are higher,

and the separation at the crossing-point to the polar state consequently larger; however the very small lifetimes of the singlet states make the actual magnitudes of quenching relatively small.

#### PHOTOSENSITIZED REACTIONS OF HYDROCARBONS

##### Reactions of Saturated Hydrocarbons

The evidence from recent investigations on the reactions of ethane,<sup>11</sup> propane<sup>12</sup> and butane<sup>13</sup> photosensitized by triplet mercury and cadmium in all cases indicates an initial carbon-hydrogen bond split. From the theoretical point of view these reactions are very similar to the reactions of hydrogen, the normal state of the hydrocarbons being a singlet state. Quenching of the physical type, the energy being taken up as vibrational energy, is again excluded by the necessity for conservation of spin angular momentum. The possibility of the hydrocarbon becoming excited to a triplet state has to be considered, but this would probably be unstable and decompose to give a hydrogen atom and a free radical. The mechanism is probably much the same as for hydrogen, reaction proceeding *via* a polar complex.

The question of whether the hydrides  $\text{HgH}$  and  $\text{CdH}$  are formed is of interest in connection with the strengths of the carbon-hydrogen bonds in the hydrocarbons;<sup>1</sup> if they are, the upper limits to the bond strength are given by the figures in the last column of Table I, while otherwise the upper limits are not so high (fourth column). It has been seen that with hydrogen the hydrides are initially formed, but that if there is sufficient energy available, as in the case of triplet mercury, the hydride decomposes at once. Presumably the situation is much the same with the saturated hydrocarbons; the hydride is formed initially but may decompose. In the absence of additional information, therefore, the upper limit to the strength of the bond

<sup>11</sup> E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.* **6**, 179 (1938); *Can. J. Research* **B16**, 303 (1938); E. W. R. Steacie and R. Potvin, *J. Chem. Phys.* **7**, 782 (1939).

<sup>12</sup> E. W. R. Steacie and D. J. Dewar, *ibid.* **8**, 571 (1940); E. W. R. Steacie, D. J. LeRoy and R. Potvin, *ibid.* **9**, 306 (1941).

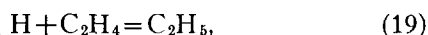
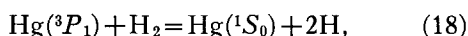
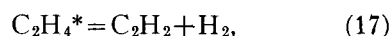
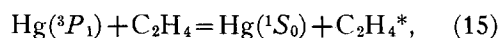
<sup>13</sup> E. W. R. Steacie and R. Potvin, *ibid.* **7**, 782 (1939).

is that which corresponds to the formation of the hydride. If, however, it could be satisfactorily proved that the hydride was not formed, the smaller figure might be accepted as a maximum.

Work has not been carried out on the reactions of saturated hydrocarbons photosensitized by singlet excited atoms, but in the light of the treatment in the preceding section there would seem to be no reason to doubt that they proceed by an initial carbon-hydrogen bond split.

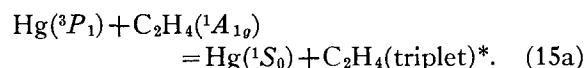
### Reactions of Ethylene

The reaction of ethylene photosensitized by triplet mercury atoms has recently been studied by LeRoy and Steacie<sup>14</sup> who obtain evidence for the following reaction scheme:



The most significant facts in favor of this mechanism are the initial pressure increase, which seems to exclude a free radical mechanism, and the increase in acetylene concentration even when the total pressure is decreasing. It is of interest to consider the first three of these reactions in the light of the present treatment.

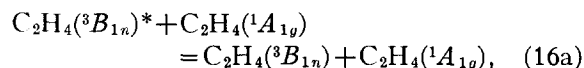
The lowest electronic state of ethylene is a singlet ( $^1A_{1g}$ ) state, and since it is known from the high quenching cross section of ethylene (cf. Table I, Part I) that reaction (15) occurs without any restriction, it follows that for conservation of spin angular momentum the excited ethylene produced in the reaction must be in a triplet state, so that reaction (15) should be written as



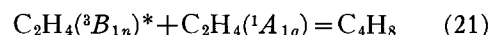
Such a triplet state, of designation  $^3B_{1n}$ , has

been shown theoretically<sup>15</sup> to lie about 20 kcal. above the normal state, the next higher being so high as to play no part here. Thus, of the 112 kcal. set free when the  $^3P_1$  mercury is deactivated, about 20 kcal. passes into electronic energy, while the majority of the remainder, about 90 kcal., goes into vibrational energy, a small amount being dissipated as translational energy. The excitation of the ethylene molecule to the triplet state is accompanied by a twisting of the double bond through  $90^\circ$ .

The second reaction, the deactivation of excited ethylene by collision with a normal molecule, takes place only with difficulty if the ethylene molecules produced are both in singlet states; however an alternative reaction,

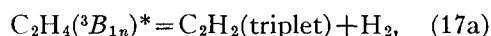


the removal of vibrational energy from the excited ethylene molecule, leaving the molecule in its triplet state, will take place with greater efficiency, although even here there will be a large negative entropy of activation<sup>16</sup> owing to the loss of rotation in the activated state.<sup>17</sup> Very little polymerization takes place so that the reaction



is apparently also slow. Since also radiation of triplet excited ethylene is restricted by the change of multiplicity, it appears that the molecule will react chiefly by splitting off hydrogen (reaction (17)).

Reaction (17) as written will be slow for the same reason, but the possibility now arises of an alternative reaction, the formation of acetylene in a triplet state:



which is not restricted by a low transition probability, but which has an activation energy higher than (17) by the excitation energy of the triplet acetylene molecule. The activation energy for the formation of unexcited acetylene and

<sup>14</sup> D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. **9**, 829 (1941); cf. H. S. Taylor and J. R. Bates, Proc. Nat. Acad. Sci. **12**, 714 (1926); J. R. Bates and H. S. Taylor, J. Am. Chem. Soc. **49**, 2438 (1927).

<sup>15</sup> J. L. Magee, W. Shand, and H. Eyring, J. Am. Chem. Soc. **63**, 677 (1941).

<sup>16</sup> R. N. Pease, J. Am. Chem. Soc. **53**, 613 (1931); H. D. Burnham and R. N. Pease, *ibid.* **62**, 453 (1940).

<sup>17</sup> F. P. Jahn, J. Am. Chem. Soc. **61**, 798 (1939).



hydrogen from unexcited ethylene has been estimated<sup>18</sup> to be 85 kcal., so that assuming the electronic excitation energy of the triplet acetylene molecule to be the same as that of triplet ethylene, or 20 kcal. (the actual magnitude is unknown), the activation energy for the formation of hydrogen and triplet acetylene from normal ethylene is about 105 kcal. It is thus clear that the excited ethylene has derived from the mercury atom sufficient energy for reaction (17a) to proceed without difficulty.

In the case of the reaction photosensitized by triplet cadmium the energy given to the ethylene, 87 kcal., is not sufficient for reaction (17a) to proceed without an activation energy. This is in accord with the results of Steacie, Potvin and LeRoy,<sup>19</sup> who find that the acetylene formation is only a small fraction of the total reaction, which is chiefly polymerization taking place with a quantum yield of only about 0.01.

The experimental facts with regard to the reaction photosensitized by singlet excited cadmium atoms are rather more difficult to interpret.<sup>20</sup> Polymerization takes place efficiently, but acetylene is a much less important product and there is no initial pressure rise. A possible explanation would seem to be that two initial mechanisms, vibrational excitation of the ethyl-

ene, which remains in its lowest electronic state, and the breaking of a carbon-hydrogen bond, are here taking place simultaneously.

### Reactions of Higher Olefines

Preliminary work<sup>21</sup> on propylene, butene-1 and butene-2 with  $^3P_1$  cadmium shows that polymerization is extremely slow. Quenching data are not available.

Of the possible initial reactions, the splitting of a carbon-hydrogen bond and the excitation of the double bond to a vibrationally-excited triplet state are the most likely. Of the two the second probably proceeds more rapidly, as is known from the larger quenching cross sections for unsaturated as compared with saturated hydrocarbons; however, subsequent reaction is difficult as polymerization proceeds only with a large negative entropy of activation,<sup>16,22</sup> and triplet cadmium does not provide enough energy for the splitting off of a hydrogen molecule.

The author wishes to express his thanks to Professor G. Herzberg, Professor R. S. Mulliken and Dr. Anthony Turkevich for information regarding molecular electronic states, and to Professor Henry Eyring, Dr. Samuel Glasstone, Dr. D. J. LeRoy and Dr. E. W. R. Steacie for valuable discussions and suggestions in connection with this and the preceding paper.

<sup>18</sup> E. W. R. Steacie, reference 1, p. 195.

<sup>19</sup> E. W. R. Steacie and R. Potvin, *Can. J. Research* **B16**, 337 (1938); **B18**, 47 (1940); E. W. R. Steacie and D. J. LeRoy, unpublished.

<sup>20</sup> E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.* **10**, 22 (1942).

<sup>21</sup> E. W. R. Steacie and D. J. LeRoy, unpublished.

<sup>22</sup> W. E. Vaughan, *J. Am. Chem. Soc.* **56**, 3863 (1932); G. B. Kistiakowsky and J. R. Lacher, *ibid.* **58**, 123 (1936); J. B. Harkness, G. B. Kistiakowsky, and W. H. Mears, *J. Chem. Phys.* **5**, 682 (1937).