

## Heats of Dissociation of CarbonHydrogen Bonds in Methane and Its Radicals

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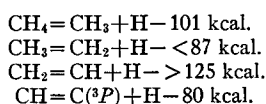
## Heats of Dissociation of Carbon-Hydrogen Bonds in Methane and Its Radicals

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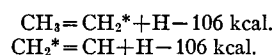
(Received March 14, 1949)

The evidence pertaining to the heat of sublimation of graphite is summarized, with the conclusion that the value of 170.6 kcal. per mole is the most probable. This figure is consistent with a value of 393 kcal. for the heat of removing the four hydrogen atoms from methane, the assignment of the heats of the successive dissociations being as follows:



The limits to the values for the second and third processes are determined on the basis of the kinetics of the reaction between sodium and methylene chloride. The methylene appearing above

is in its lowest state, a singlet state in which the bonding to the hydrogen atoms is through  $p$ -orbitals of atomic carbon, the bond containing a certain amount of ionic character. It is suggested that the formation of  $\text{CH}_2$  in a triplet excited state, in which the bonding to the hydrogen atoms is through  $sp$  hybrid orbitals of atomic carbon, corresponds to the following thermochemical values:



From this suggestion it follows that the energy of excitation of the methylene "molecule," the lowest state (singlet), to the methylene "diradical," the triplet excited state, is at least 19 kcal. The evidence for the existence of the two states is discussed.

## INTRODUCTION

THERE has now accumulated a considerable amount of evidence which points to the following mutually consistent thermochemical values:

$$\text{C}_{\text{graphite}} = \text{C}_{\text{gas}}(^3P) - 170.6 \text{ kcal.} \quad (1)$$

$$\text{CO}(^1\Sigma^+) = \text{C}_{\text{gas}}(^3P) + \text{O}(^3P) - 256 \text{ kcal.} \quad (2)$$

$$\text{C}_{\text{gas}}(^3P) + 4\text{H}(^2S) = \text{CH}_4 + 393 \text{ kcal.} \quad (3)$$

In support of these figures are the following facts:

(1) The most reliable direct determinations of the heat of sublimation of graphite, involving both static and dynamic methods, give a value in the neighborhood of 170 kcal.; some of the results are summarized in Table I. It may be mentioned that in 1924 Kohn and Gückel<sup>1</sup> obtained a value of 147 kcal., but that this is inconsistent with other direct measurements and with the spectroscopic data, to be considered later. The first reliable value is that of Marshall and Norton,<sup>2</sup> while the recent value of Brewer, Gilles, and Jenkins<sup>3</sup> appears to be very accurate.<sup>4</sup>

(2) The spectrum of carbon monoxide leaves a choice between the values of 256.1, 210.8, and 159.7 kcal. for the heat of dissociation,  $D(\text{CO})$ , of carbon monoxide into  $\text{C}(^3P)$  and  $\text{O}(^3P)$ .<sup>5</sup> This heat of dissociation can be related to the heat of sublimation of graphite by the following well-established thermochemical relations:<sup>6</sup>

$$\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_2 = \text{CO} + 27.2 \text{ kcal.,} \quad (4)$$

$$\frac{1}{2}\text{O}_2 = \text{O} - 58.6 \text{ kcal.,} \quad (5)$$

and the heats of sublimation so calculated on the basis of the three spectroscopic values for  $D(\text{CO})$  are given in Table II. The heat of reaction (3) can be calculated from the heat of sublimation using the following values:<sup>6</sup>

$$\text{C}(\text{graphite}) + 2\text{H}_2 = \text{CH}_4 - 16.0 \text{ kcal.,} \quad (6)$$

$$\text{H}_2 = 2\text{H} - 103.2 \text{ kcal.} \quad (7)$$

The possible values for reaction (3) consistent with the possible spectroscopic values for  $D(\text{CO})$  are included in Table II. Of the three spectroscopic values for  $D(\text{CO})$ , the second, 210.8 kcal., was favored by G. Herzberg,<sup>5</sup> but A. G. Gaydon and W. G. Penney<sup>7</sup> have pointed out

TABLE I. Heats of sublimation of graphite.

Authors	Type of method	Heat of sublimation
Marshall and Norton*	dynamic	177 kcal.
Brewer, Gilles, and Jenkins**	static	170.4 kcal.

\* See reference 2.

\*\* See reference 3.

TABLE II. Equivalent thermochemical values.

$D(\text{CO})$ per mole	Heat of sublimation of graphite per mole	Heat of formation of $\text{CH}_4$ from $\text{C}(^3P)$ and $4\text{H}(^2S)$
256.1 kcal. (11.11 ev)	-170.6 kcal.	+393.1 kcal.
210.8 kcal. (9.14 ev)	-125.0 kcal.	+347.5 kcal.
157.9 kcal. (6.92 ev)	-72.1 kcal.	+294.6 kcal.

\* Now a Postdoctoral Fellow of the National Research Council of Canada, Ottawa, Ontario.

<sup>1</sup> Kohn and Gückel, *Zeits. f. Physik* **27**, 305 (1924).

<sup>2</sup> A. L. Marshall and F. J. Norton, *J. Am. Chem. Soc.* **55**, 431 (1924).

<sup>3</sup> Brewer, Gilles, and Jenkins, *J. Chem. Phys.* **16**, 797 (1948).

<sup>4</sup> This value has been criticized by L. H. Long, *J. Chem. Phys.* **16**, 1078 (1948), whose arguments have been answered by L. Brewer, *J. Chem. Phys.* **16**, 1165 (1948).

<sup>5</sup> G. Herzberg, *Chem. Rev.* **20**, 145 (1947).

<sup>6</sup> All thermochemical values are referred to 0°K, and are taken from *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards publication.

<sup>7</sup> A. G. Gaydon and W. G. Penney, *Proc. Roy. Soc. A* **183**, 347 (1945); A. G. Gaydon, *Dissociation Energies* (Chapman and Hall, Ltd., London, 1947).

that if the non-crossing rule for potential-energy curves of the same multiplicity holds, the value 256.1 kcal. must be accepted. This is a compelling argument, as the non-crossing rule has a sound theoretical basis,<sup>8</sup> and does not appear to be violated by any other molecule.

(3) N. V. Sidgwick and H. D. Springall<sup>9</sup> have shown that the strengths of the C-Hg links in  $\text{Hg}(\text{CH}_3)_2$ ,  $\text{Hg}(\text{C}_2\text{H}_5)_2$ , and  $\text{Hg}(\text{C}_6\text{H}_5)_2$ , together with thermochemical data, provide evidence for the set of highest values.

(4) Calculations by G. J. Kynch and W. G. Penney<sup>10</sup> of the excitation energies of benzene, butadiene, and hexatriene lead to the same set of highest values.

On the other hand, some objections to this set of highest values have been suggested. Herzberg, Herzfeld, and Teller<sup>11</sup> suggested that the activation energy for the sublimation of carbon may be about 1.5 times the energy of dissociation; this could lead to the value of 125 kcal. for the heat of sublimation. However, this argument cannot apply to the equilibrium measurements of Brewer *et al.* Another objection relates to the possibility that the carbon in the above equations should be in the tetravalent ( $^5S$ ) state: these arguments will now be considered.

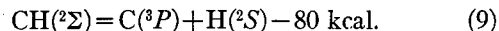
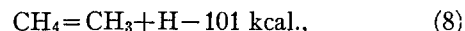
#### THE TETRAVALENT ( $^5S$ ) CARBON ATOM

In discussing this problem a number of authors<sup>12,13</sup> have concluded that since tetravalent carbon compounds may be regarded as being related to the carbon in an excited ( $^5S$ ) state, in which a  $2s$  electron has been promoted to the  $2p$  orbital to give the configuration  $(1s)^2(2s)(2p)^3$ , the carbon atom occurring in Eqs. (1), (2), and (3) must be regarded as being in the  $^5S$  state. In particular, Long and Norrish<sup>13</sup> have postulated that the  $^5S$  state is 65 kcal. higher than the lowest state, ( $^3P$ ), and taking the heat of sublimation of carbon to be 190 kcal., obtain  $190 - 65 = 125$  kcal. for the heat of sublimation to the  $^3P$  state. By the same argument the energy of dissociation of carbon monoxide to  $\text{C}(^3P)$  and  $\text{O}(^3P)$  is reduced to about 210 kcal., which has been seen to correspond to one of the values suggested by spectroscopic data. However, there are serious difficulties associated with this interpretation: (1) this argument of Long and Norrish was originally advanced to explain Marshall and Norton's value for the heat of sublimation, which, involving a rate measurement, in reality is the energy of activation of the sublimation process: this value might, therefore, refer to the formation of carbon in an intermediate  $^5S$  state, which subsequently falls to

the ground state with emission of radiation. The argument is not applicable to equilibrium experiments, in which it can hardly be supposed that  $^5S$  carbon is involved. (2) Even if the equilibrium measurements were discounted, there remains a serious objection to the supposition that carbon sublimates to the  $^5S$  state. The energy of excitation of  $\text{C}(^3P)$  to the ( $^5S$ ) state is now known to be 95.9 kcal.;<sup>14</sup> the assumption that graphite sublimates to the  $^5S$  state with heat of 170 kcal./mole reduces the heat of sublimation to the  $^3P$  state to 74 kcal., which would require a much higher vapor pressure than has ever been recorded. (3) The fact that carbon when tetravalent can be regarded as in a  $^5S$  state does not imply that when dissociation occurs the carbon remains in this state; in fact, such an assumption is contrary to what is known about the mechanisms of non-adiabatic reactions.<sup>15</sup> This can be seen most easily for the diatomic molecule CO, the electronic states of which have been discussed by Gaydon and Penney.<sup>7</sup> Although the carbon atom is in the tetravalent state, the lowest state of the molecule CO is ( $^1\Sigma^+$ ), and this dissociates into  $\text{C}(^3P)$ . This argument applies equally well to the more complicated situation existing when solid carbon is sublimed; the lowest potential energy surface for solid carbon, although correlating with  $\text{C}(^5S)$ , will actually give rise to  $\text{C}(^3P)$  when dissociation of the bonds in solid carbon occurs.

#### DISSOCIATION ENERGIES OF METHANE AND ITS RADICALS

On the basis of the conclusion, which has been seen to be very highly probable, that the value of 393 kcal. refers to the complete dissociation of methane into  $\text{C}(^3P)$  and  $4\text{H}(^2S)$ , it remains to consider how this figure should be divided among the individual steps. Of the four processes corresponding to the successive removal of hydrogen atoms, the heats of two, the first and last, are known with some certainty. The values are as follows:



The first of these figures was obtained by G. B. Kistiakowsky *et al.*<sup>16</sup> using a kinetic procedure involving the bromination of methane. Support for this value is rendered by the work of Polanyi *et al.* on the pyrolysis of methyl iodide<sup>17</sup> and by Stevenson's electron impact

<sup>8</sup> J. von Neumann and E. P. Wigner, *Physik. Zeits.* **30**, 467 (1927).

<sup>9</sup> N. V. Sidgwick and H. D. Springall, *Nature* **156**, 599 (1945).

<sup>10</sup> K. G. Kynch and W. G. Penney, *Proc. Roy. Soc. A* **179**, 214 (1941).

<sup>11</sup> Herzberg, Herzfeld, and Teller, *J. Phys. Chem.* **41**, 325 (1937).

<sup>12</sup> R. Schmid and L. Gero, *Zeits. f. physik. Chemie* **B36**, 105 (1937).

<sup>13</sup> L. H. Long and R. G. W. Norrish, *Nature* **157**, 468 (1946); *Proc. Roy. Soc. A* **187**, 337 (1946).

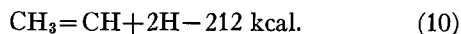
<sup>14</sup> A. G. Shenstone, *Phys. Rev.* **72**, 411 (1947); cf., B. Edlen, *Zeits. f. Physik* **84**, 746 (1933); *Nature* **159**, 129 (1947); R. F. Backer and S. Goudsmit, *Phys. Rev.* **46**, 948 (1934).

<sup>15</sup> Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), Chapter VI.

<sup>16</sup> Andersen, Kistiakowsky, and Van Artsdalen, *J. Chem. Phys.* **10**, 305 (1942); E. R. Van Artsdalen, *J. Chem. Phys.* **10**, 653 (1942); H. G. Andersen and G. B. Kistiakowsky, *J. Chem. Phys.* **11**, 6 (1943); G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.* **12**, 469 (1944).

<sup>17</sup> E. T. Butler and M. Polanyi, *Nature* **146**, 129 (1940); *Trans. Faraday Soc.* **39**, 19 (1943); E. C. Baughan and M. Polanyi,

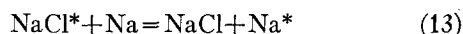
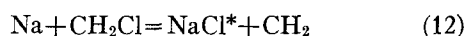
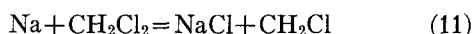
data.<sup>18</sup> The second value, 80.0 kcal., for the heat of dissociation of CH in its lowest state ( $^2\Sigma$ ) was obtained by G. Herzberg<sup>19</sup> from spectroscopic data. These two values, together with the value 393 kcal. for the complete dissociation of methane, lead to



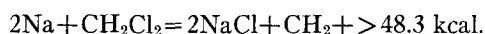
It now remains to consider how the value 212 kcal. is to be divided between the processes  $\text{CH}_3 = \text{CH}_2 + \text{H}$  and  $\text{CH}_2 = \text{CH} + \text{H}$ .

### The Methylene Radical

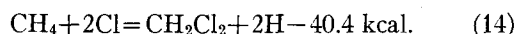
The only positive experimental information that we have been able to discover regarding the energy of the lowest state of  $\text{CH}_2$  is found in the work of C. E. H. Bawn and W. J. Dunning,<sup>20</sup> and this gives only a lower limit to the energy of dissociation of the  $\text{CH}_2$  molecule. These workers found that the reaction between sodium vapor and methylene chloride is strongly chemiluminescent, emitting the sodium *D* line. By analogy with many other reactions of this type,<sup>21</sup> the mechanism is most probably



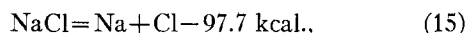
in which scheme the sodium chloride molecule  $\text{NaCl}^*$  is vibrationally excited and the sodium atom  $\text{Na}^*$  is electronically excited. Since electronic excitation of sodium requires 48.3 kcal., it follows that reactions (11) and (12), with the formation of normal  $\text{NaCl}$ , must jointly be exothermic by at least this amount; that is,



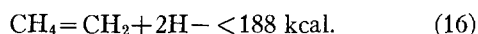
This equation, together with



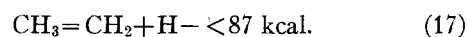
and



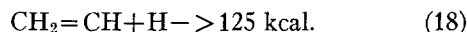
gives rise to



With Eq. (8) this gives



and



Nature **146**, 685 (1940); Trans. Faraday Soc. **37**, 648 (1941); E. C. Baughan, Nature **147**, 542 (1941); Baughan, Evans, and Polanyi, Trans. Faraday Soc. **137**, 377 (1941).

<sup>18</sup> D. P. Stevenson, J. Chem. Phys. **10**, 291 (1942); J. Am. Chem. Soc. **65**, 209 (1943); D. P. Stevenson and J. A. Hipple, J. Am. Chem. Soc. **64**, 1588, 2766 (1942); J. A. Hipple and D. P. Stevenson, Phys. Rev. **63**, 121 (1943).

<sup>19</sup> G. Herzberg, *Molecular Spectra and Molecular Structure I, Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939).

<sup>20</sup> C. E. H. Bawn and W. J. Dunning, Trans. Faraday Soc. **35**, 185 (1939).

<sup>21</sup> See M. Polanyi, *Atomic Reactions* (Williams and Norgate, London, 1932).

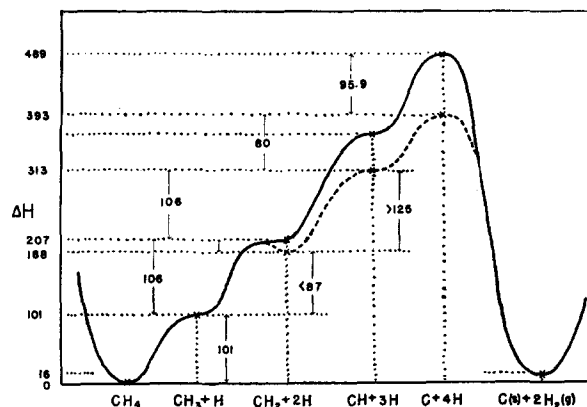


Fig. 1. Schematic representation of the energy levels of  $\text{CH}_4$  and its radicals with respect to the gaseous carbon and hydrogen atoms.

Although only a lower limit to the energy of dissociation of methylene has been determined, the results imply that the  $\text{CH}_2$  is considerably more stable with respect to removal of a hydrogen atom than is  $\text{CH}_3$ . This is consistent with our previous conclusion,<sup>22</sup> arrived at on the basis of the shape,<sup>23</sup> that the lowest state of methylene is a singlet state in which the bonds to hydrogen are formed by *p*-orbitals of carbon, and have considerable ionic character. This means that when an additional hydrogen atom is added to  $\text{CH}_2$ , promotion of a carbon *2s* electron to a *2p* atomic orbital must occur, followed by *sp*<sup>2</sup> hybridization. The stability due to hybridization is not sufficient to offset the energy required for promotion, so that  $\text{CH}_3$  is less stable to dissociation into  $\text{CH}_2 + \text{H}$  than is  $\text{CH}_2$  to dissociation into  $\text{CH} + \text{H}$ . It is to be noted that this point of view differs from that of A. D. Walsh,<sup>24</sup> who has recently discussed the problem: according to him  $\text{CH}_2$  is in a triplet state in which each hydrogen atom is held to the carbon through a carbon *sp* hybrid atomic orbital. This interpretation necessitates that promotion occur during the reaction  $\text{CH} + \text{H} = \text{CH}_2$  rather than during the reaction  $\text{CH}_2 + \text{H} = \text{CH}_3$ . It appears that our interpretation is preferable in view of the fact that it is consistent not only with the shape of  $\text{CH}_2$  but also with the results of Bawn and Dunning.

The energy levels of  $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$ , and  $\text{C}$  with respect to methane are represented schematically in Fig.

TABLE III. Heats of dissociation.

Reaction	Values proposed above ( <i>L</i> = 170)	Vogel's values ( <i>L</i> = 170)	Values using ( <i>L</i> = 125)	Vogel's values ( <i>L</i> = 125)
$\text{CH}_4 = \text{CH}_3 + \text{H}$	101	109	101	101
$\text{CH}_3 = \text{CH}_2 + \text{H}$	<87	124	<87	87
$\text{CH}_2 = \text{CH} + \text{H}$	>125	80	>80	80
$\text{CH} = \text{C} + \text{H}$	80	80	80	80

<sup>22</sup> K. J. Laidler and E. J. Casey, J. Chem. Phys. **17**, 213 (1949).

<sup>23</sup> G. Herzberg, Rev. Mod. Phys. **14**, 195 (1942).

<sup>24</sup> A. D. Walsh, Faraday Soc. Discussion **2**, 18 (1947).

1, some of the features of which are suggested by the electronic configurations of the radicals and of analogous molecules; these will be discussed later.

### THE EXCITED METHYLENE RADICAL

On surveying the literature concerning the reactions of the methylene radical, one is struck by the inconsistencies in behavior depending upon the manner in which the radical is produced. In our opinion these differences are due to the fact that methylene is produced sometimes in the singlet ground state, and is relatively unreactive, and sometimes in the triplet excited state, and is highly reactive. Thus Pearson, Purcell, and Saigh,<sup>25</sup> producing methylene from diazomethane at 450°C, found that the radical has a comparatively long life, and concluded from this that it is in a singlet state. Belchetz and Rideal<sup>26</sup> found  $\text{CH}_2$  at a distance less than the mean free path from a hot carbon filament in methane, and F. O. Rice and A. L. Glasebrook<sup>27</sup> found no  $\text{CH}_2$  at greater distances; the  $\text{CH}_2$  so formed is apparently more reactive than that in the work of Pearson *et al.*, and is probably in the excited triplet state, a diradical. Recent work of R. G. W. Norrish<sup>28</sup> has indicated high reactivity, presumably because the  $\text{CH}_2$  was produced in the excited state.

The high reactivity of methylene in the excited state indicates that reactions such as

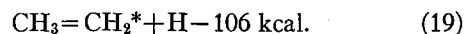


must have little activation energy and hence be not endothermic; together with Eq. (8) this implies that the reaction  $\text{CH}_3 = \text{CH}_2^* + \text{H}$  must be endothermic by at least 102 kcal.

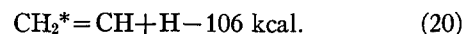
A further indication as to the energy level of the excited methylene diradical may be obtained on the basis of the analogy between the C—H bond in the methyl radical and the C—H bond in ethylene, in both of which structures the carbon atom has  $sp^2$  hybridization. This means that the removal of a hydrogen atom from  $\text{CH}_3$  to give  $\text{CH}_2$  in the triplet state might be expected to require approximately the same energy as is necessary to remove a hydrogen atom from  $\text{C}_2\text{H}_4$  to give the excited ethylidene radical, in which the C=C—H angle is 180°.

The force constant of the C—H bond in a molecule is derived from the curvature of the potential-energy surface near its position of minimum energy. The lowest stable state of  $\text{C}_2\text{H}_4$  is known to contain carbon atoms which are in a hybridized  $^5S$  state; in such a molecule the C—H bond vibrational energy levels in the vicinity of minimum energy are such as to be related to dissocia-

tion products in which the unsaturated carbon atom is still in the  $^5S$  state. Hence, the C—H force constant in ethylene is related to excited ethylidene  $\text{CH}_2 = \text{C} - \text{H}$ , in which the unsaturated carbon atom forms two  $sp$  hybrid orbitals, diametrically opposed, a structure clearly analogous to that of  $\text{CH}_2^*$ , the methylene diradical. On the basis of the C—H force constant and interatomic distance in ethylene, a value of  $\sim 106$  kcal. for the dissociation energy of the bond has been deduced; this then very probably refers to the dissociation to give  $\text{C}_2\text{H}_3$  in the triplet excited state. By this analogy, then, we tentatively assume that this value also applies to the dissociation of the methyl radical to give methylene in the triplet excited state, viz.



This value leads to the relation



From this it follows that the energy of excitation of the methylene molecule to the triplet excited state, the diradical, is at least 19 kcal.

### POTENTIAL ENERGY SURFACE FOR THE COMPLETE DISSOCIATION OF METHANE

These values for the successive heats of dissociation of methane and its radicals may be used to construct a schematic potential-energy surface for the complete dissociation of methane; this is shown in Fig. 1. In this diagram, surfaces related to carbon in the  $^5S$  state are represented by full lines, and those for carbon in the  $^3P$  state by broken lines. It is to be noted that carbon in methane and in methyl is necessarily in the  $^5S$  state, but that when a hydrogen is removed from  $\text{CH}_3$  the lowest state of  $\text{CH}_2$  is reached by a crossing over to the singlet state, in which the carbon is in the  $^3P$  state; this will probably involve a potential energy maximum between  $\text{CH}_3$  and  $\text{CH}_2$ . It follows from this that there will be an activation energy associated with the addition of a hydrogen atom to  $\text{CH}_2$  in the ground state. The addition of hydrogen to  $\text{C}(^3P)$ ,  $\text{CH}$ ,  $\text{CH}_3$ , and to  $\text{CH}_2$  in the excited state will, however, probably not require any activation energy.

The scheme proposed here differs from previous ones in various respects. It differs from those of Gero,<sup>12</sup> Long and Norrish,<sup>13</sup> and Walsh,<sup>24,29</sup> in accepting the value of 170 kcal. as applying to the heat of sublimation of graphite to give  $^3P$  carbon. It further differs from that of Walsh<sup>24</sup> in that the lowest state of  $\text{CH}_2$  is taken to be the singlet state, containing  $^3P$  carbon; according to Walsh, the transition  $\text{C}(^5S) \rightarrow \text{C}(^3P)$  occurs at  $\text{CH}_2 \rightarrow \text{CH}$ . Reference may also be made to the recent papers of Gero and Valatin,<sup>30</sup> who assume the energy of the C—H bond in  $\text{CH}_2$  to be the same as that of the secondary

<sup>25</sup> Pearson, Purcell, and Saigh, J. Chem. Soc. 409 (1938).

<sup>26</sup> Belchetz, Trans. Faraday Soc. 30, 170 (1934); Belchetz and Rideal, J. Am. Chem. Soc. 56, 1168 (1935); *ibid.*, p. 2466.

<sup>27</sup> F. O. Rice and A. L. Glasebrook, J. Am. Chem. Soc. 56, 2381 (1934).

<sup>28</sup> R. G. W. Norrish and G. Porter, Faraday Soc. Discussions 2, 96 (1947).

<sup>29</sup> A. D. Walsh, Trans. Faraday Soc. 43, 60 (1947).

<sup>30</sup> L. Gero, J. Chem. Phys. 16, 1011 (1948); L. Gero and J. G. Valatin, *ibid.* 16, 1014 (1948); J. G. Valatin, *ibid.* 16, 1018 (1948).

bonds of hydrocarbons; since the carbon atoms in the latter have  $sp^3$  hybridization while the carbon in CH<sub>2</sub> binds hydrogens through  $p$  atomic orbitals, there is clearly no justification for this view.

Voge<sup>31</sup> has made quantum-mechanical calculations of the C-H bond strengths, obtaining values which are not consistent with the present values. Such calculations can be expected to give only orders of magnitude when it is remembered the assumptions which have to be made. The present conclusions, being based on a

<sup>31</sup> H. H. Voge, J. Chem. Phys. 4, 581 (1936); 16, 984 (1948).

theoretical interpretation of reliable experimental data, seem to us to have a firmer basis than conclusions arrived at on the basis of purely theoretical computations. However, it must be mentioned that the acceptance of 125 kcal. for the heat of sublimation of carbon would have led us to a set of values which are quite consistent with those favored by Voge. This might be regarded as an argument in favor of the lower value, but in view of the points raised earlier we prefer the higher one. Our results and those of Voge are listed for comparison in Table III.

## Role of Hydrogen Peroxide in the Thermal Combination of Hydrogen and Oxygen

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Hydrogen peroxide was identified as an intermediate product in the steady thermal combination of hydrogen and oxygen near 540°C by an examination of the absorption spectrum of the reacting mixture. The absorption at a particular wave-length (2537Å) was then used in a quantitative study of the variation of hydrogen peroxide concentration in the reacting mixture as a function of conditions. The results obtained were compared with those obtained by chemical analysis of the gas mixture. The commonly accepted mechanism of the reaction proposed by Lewis and von Elbe is applied to the interpretation of the results obtained.

### I. PROBLEM

THE reaction mechanism of the thermal combination of hydrogen and oxygen to form water has been the subject of a very considerable amount of work in recent years. An important part of this work has been the investigation of the intermediate products of the reaction, since an accurate knowledge of what these products are and the relative role and importance of each of them is necessary to an adequate reaction theory. Previous work indicated two definite facts concerning the thermal combination of hydrogen and oxygen at a total pressure of about one atmosphere and at temperatures in the vicinity of 540°C; first, that free hydroxyl (which might logically have been expected as an important intermediate product) does not accumulate in the reaction mixture to an appreciable extent,<sup>1</sup> and second, that hydrogen peroxide is present in fairly large amounts in the exit gases when a mixture of hydrogen and oxygen is passed through a hot reaction vessel under proper conditions.<sup>2</sup>

At the time the present investigation was undertaken, there was no very reliable basis for deciding whether or not the hydrogen peroxide found in the exit gases was present as such in the reacting mixture. Early studies

of the thermal decomposition of hydrogen peroxide vapor<sup>3</sup> had indicated an appreciable decomposition even at temperatures below 100°C, although more recent studies<sup>4</sup> showed that, under proper conditions, the molecule is relatively stable to much higher temperatures in the presence of oxygen or nitrogen, but undergoes a reaction with hydrogen at elevated temperatures. Furthermore, it had been noted that the hydrogen peroxide observed as a result of pumping out the products of an electrical discharge through water vapor<sup>5</sup> is undoubtedly formed as a result of the combination of active radicals *in the trap* used to collect the products. As we have reported previously,<sup>6</sup> however, hydrogen peroxide has been identified with virtual certainty in the reacting mixture by observing the absorption spectrum while the reaction was proceeding. In addition hydrogen peroxide has been identified by means of its absorption spectrum as an intermediate product in the

<sup>3</sup> L. W. Elder and E. K. Rideal, Trans. Faraday Soc. 23, 545 (1927); C. N. Hinshelwood and C. R. Prichard, J. Am. Chem. Soc. 123, 2725 (1923); G. B. Kistiakowsky and S. L. Rosenberg, J. Am. Chem. Soc. 59, 422 (1937); and E. Kondrat'eva and V. N. Kondrat'ev, J. Phys. Chem. USSR 19, 178 (1945).

<sup>4</sup> E. J. Harris, Trans. Faraday Soc. 44, 764 (1948); see also forthcoming article by C. K. McLane in this journal.

<sup>5</sup> W. H. Rodebush and R. W. Campbell, J. Chem. Phys. 4, 293 (1936) and K. H. Geib, J. Chem. Phys. 4, 391 (1936); Rodebush, Keizer, McKee, and Quagliano, J. Am. Chem. Soc. 69, 538 (1947).

<sup>6</sup> R. B. Holt and O. Oldenberg, Phys. Rev. 71, 479 (1947).

<sup>1</sup> Oldenberg, Morris, Morrow, Schneider, and Sommers, Jr., J. Chem. Phys. 14, 66 (1946).

<sup>2</sup> R. N. Pease, J. Am. Chem. Soc. 52, 5106 (1930) and 53, 3188 (1931).