

The Mechanism of Processes Initiated by Excited Atoms III. PhotoSensitized Hydrocarbon Reactions

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3.3. Cross Section for Formation of the 40-hr. As^{77}

The cross-section of Ge for formation of the 12-hr. Ge^{77} by an (n, γ) process was determined to be 0.0055 barn by Seren, Sturm, and Moyer.¹² Since the 40-hr. As^{77} is formed in two ways, from 12-hr Ge^{77} and 59-sec. Ge^{77} , its formation cross section is the sum of the cross sections of the 12-hr. Ge^{77} and the 59-sec. Ge^{77} , whose cross section was found to be about 10 percent higher than that of 12-hr. Ge^{77} in these experiments, or 0.011 barn. The cross section of 0.0155 barn given by Seren *et al.* for the formation of the 40-hr. Ge^{77} is undoubtedly too high since it contains the contribution of the 40-hr. As^{77} (0.011 barn), an activity which was found after the Ge cross section work was done.

3.4. Summary of Ge-As Experiments

The presence of a short-lived state of Ge^{77} decaying by β^- -emission to 40-hr. As^{77} has been

¹² L. Seren, W. Sturm, and W. Moyer, Metallurgical Laboratory Report CP-1389, February 24, 1944.

shown by As extractions of GeS_3 solutions irradiated with neutrons. The cross section for formation of the short-lived state was found to be about 10 percent larger than that of the 12-hr. Ge^{77} . A short-lived Ge activity was found by irradiating GeS_2 with neutrons for 20 sec. and measuring the activity through Al absorbers. The half-life was determined to be 59 ± 2 sec. and the β -energy, 2.8 Mev. The agreement between the cross sections for formation of the 59-sec. Ge and the 40-hr. As^{77} from the short-lived Ge^{77} makes it probable that the 59-sec. Ge is genetically related to the 40-hr. As^{77} .

The presence of the 59-sec. Ge^{77} activity decaying by β^- -emission to 40-hr. As^{77} resolves the difficulty of the apparently high "independent" yield of As^{77} in fission on the assumption that the excess fission yield of As^{77} is due to 59-sec. Ge^{77} .

This document is based on work performed at the Argonne National Laboratory, Chicago, Illinois, operated by the University of Chicago for the Atomic Energy Commission.

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The Mechanism of Processes Initiated by Excited Atoms

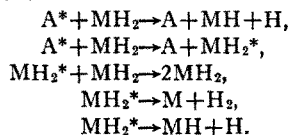
III. Photo-Sensitized Hydrocarbon Reactions

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The photo-sensitized reactions of the hydrocarbons are discussed in terms of the following reaction scheme, in which A^* indicates the photo-sensitizing atom and MH_2 the hydrocarbon:



The first and fifth reactions are followed by polymerizations. Expressions for the quenching rate, the rate of formation of M, and the rate of formation of polymer, are obtained in terms of the original rate constants, and a

number of special cases of practical interest are treated. The relative rates of the reactions are discussed with reference to the experimental data, particular regard being paid to the energy relationships, the general kinetic behavior, and the influence of temperature. Evidence is adduced in favor of the following: (1) the strength of the C-H bond in ethylene is about 100 kcal., (2) there is a triplet-excited state of acetylene with an excitational energy of 10-30 kcal., (3) conversion of a large amount of electronic energy into vibrational energy proceeds with difficulty, the process taking place much more readily when some of the energy can be taken up as electronic energy of the colliding molecule.

INTRODUCTION

APPLICATIONS of the theory of chemical change to the elucidation of reaction mechanisms have for the most part followed one of two

general paths. The first of these consists of the detailed quantum-mechanical calculation of the rates of simple processes, and the comparison of the results with experiment; the second is the

analysis of reactions, or of groups of homologous reactions, with the aid of the general theory. One class of reactions which are more amenable to analysis in the light of theory, that is, to the second type of treatment, comprises the photo-sensitized reactions of the hydrocarbons. The investigations on these have been recently reviewed by Steacie,¹ in whose laboratory much of the work on them has been done. The quantum-mechanical theory of molecular structure permits the qualitative construction of the potential energy surfaces upon which reaction must take place, and with the aid of these alone it is possible to arrive at a number of significant conclusions regarding the manner in which the reactions occur. Some simplification is provided by the fact that most of the reactions take place with zero activation energy, and that many reaction mechanisms are excluded by the necessity of conservation of spin angular-momentum. Preliminary remarks on these reactions have already been published (Part II),² and the object of the present paper is to show that now that much information has accumulated on the reactions of the simpler hydrocarbons, the theoretical analysis is consistent with, and supplements, the conclusions directly derived from experiment.

The experimental work on quenching and photo-sensitization has been done mainly with the metals sodium, zinc, cadmium, and mercury, and in the case of the last three has involved transitions to the ground state (1S_0) from both singlet-excited (1P_1) and triplet-excited (3P_1) states. The details of these transitions are given in Table I, which includes the energy liberated in transition to the normal state (fourth column),

TABLE I. Energies of excitation, and available energies, in electronic transitions.

Metal	Transition	Line (Å)	Energy of excitation (kcal.)	Energy of formation of hydride (kcal.)	Total available energy (kcal.)
Sodium	$3^2P - 2^2S_1$	{5890} {5896}	48.3	51.6	99.9
Zinc	$4^3P_1 - 4^1S_0$	3076	92.5	23.1	115.6
Zinc	$4^1P_1 - 4^1S_0$	2139	133.4	23.1	156.5
Cadmium	$5^3P_1 - 5^1S_0$	3261	87.3	15.5	102.8
Cadmium	$5^1P_1 - 5^1S_0$	2288	124.4	15.5	139.9
Mercury	$6^3P_1 - 6^1S_0$	2537	112.2	8.5	120.7
Mercury	$6^1P_1 - 6^1S_0$	1849	153.9	8.5	162.4

¹ E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946), Chapters IV and VI.

² K. J. Laidler, *J. Chem. Phys.* 10, 43 (1942).

TABLE II. Bond strengths.

Bond	Strength (kcal.)
H-H	103.8
CH ₃ -H	102
C ₂ H ₅ -H	97
H ₂ C:CH-H	100 ^a
CH ₂ :CHCH ₂ -H	92
HC:C-H	104
CH ₃ -CH ₃	86
CH ₃ -C ₂ H ₅	84

^a This value is discussed later.

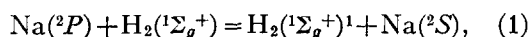
the heat of formation of the hydride, AH, of the metal A (fifth column), and the sum of these two (last column). The latter figures represent the energy available if, in addition to de-activation to the normal state, the hydride is formed; evidence for the production of the hydrides in these reactions has in some cases been obtained by the detection of their resonance bands. The interactions of most of these excited atoms with hydrogen, ethane, and ethylene, have been studied, and the results interpreted in a general way in terms of the strengths of the bonds which have to be broken.¹ These bond strengths are not known with great certainty, but a set that may be accurate within 1 or 2 kcal. is given in Table II.

Excited sodium (2P) occupies an exceptional position in that, owing to its comparatively low energy of excitation, it does not in general bring about chemical reaction; it is, however, quenched by hydrogen and the hydrocarbons. Excited zinc, cadmium, and mercury, in both triplet and singlet states, are also quenched by hydrogen which is at the same time dissociated into atoms. With ethane an analogous splitting of the carbon-hydrogen bond takes place, the atom and radical formed bringing about various polymerization reactions. With ethylene and the other unsaturated hydrocarbons the results are much more complicated and show considerable variation according to the excited atom used. It appears that reaction may proceed by two distinct primary mechanisms, one initiated by a carbon-hydrogen bond split and the other by the formation of an excited olefin molecule; however in individual cases one or both of these reaction mechanisms may fail to occur. The facts outlined above have been rather firmly established by experiment, and the evidence for them is

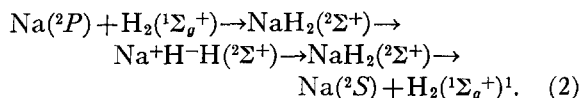
presented in Steacie's book; their interpretation in the light of theory, particularly of the relative rates of the reactions, is the purpose of the present paper.

Previous theoretical discussions of reactions involving excited electronic states in terms of specific potential-energy surfaces³ have been presented by Magee,⁴ who discussed chemi-luminescent reactions, by Magee and Ri,⁵ who treated the quenching of sodium by hydrogen, and by the present writer, who treated the quenching of sodium by the inert gases, hydrogen and the halogens (Part I),⁶ and the photo-sensitization of hydrogen by excited mercury and cadmium (Part II).² The results obtained with hydrogen are of significance in connection with the hydrocarbon reactions, and will therefore be described briefly.

The quenching of excited (²P) sodium by hydrogen is necessarily a physical process; the over-all reaction may be written as

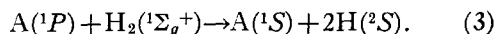


in which $\text{H}_2(^1\Sigma_g^+)^1$ denotes hydrogen in its lowest electronic state but containing excess energy which is probably chiefly in the form of vibrational energy. Detailed study of the potential-energy surfaces^{6,6} indicates that the system reaches its final state *via* a polar complex which may be denoted as $\text{Na}^+\text{H}-\text{H}$, and that the reaction path may be written as follows:



In this scheme the second $\text{NaH}_2(^2\Sigma^+)$ state is a lower state than the first, and it has not quite sufficient energy (see Tables I and II) to form NaH and H .

With singlet mercury and cadmium atoms there is sufficient energy to break the $\text{H}-\text{H}$ bond, and the over-all reaction is:



This process again will proceed *via* a polar state,

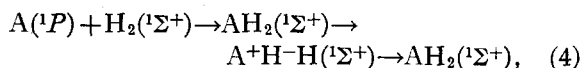
³ For a review of the earlier work see S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, 1941).

⁴ J. L. Magee, *J. Chem. Phys.* **8**, 687 (1940).

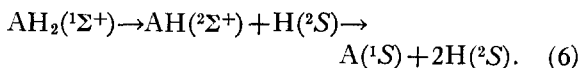
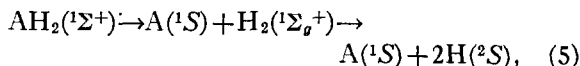
⁵ J. L. Magee and T. Ri, *J. Chem. Phys.* **9**, 638 (1941).

⁶ K. J. Laidler, *J. Chem. Phys.* **10**, 34 (1942).

the steps being:

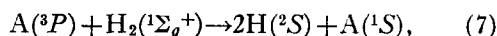


the latter AH_2 complex being in a lower state than the former, and decomposing by one of two alternative processes:

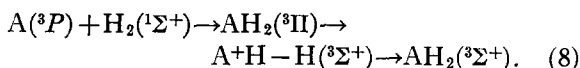


In either case the H_2 or AH produced will have sufficient vibrational energy to decompose at once into the free atoms.

The situation with the triplet atoms is different, owing to the difference in multiplicity between initial and final states. The hydrogen can no longer emerge from the reaction in its lowest electronic state, but only as free atoms. The over-all change is therefore:



and the detailed mechanism is:



The $\text{AH}_2(^3\Sigma^+)$ can now decompose into $\text{AH}(^2\Sigma^+)$ and $\text{H}(^2S)$ by a process analogous to (6), the AH then splitting into $\text{A}+\text{H}$, but the reaction analogous to (5) is now forbidden by the rule of conservation of spin angular-momentum. The reaction can only involve the splitting of the $\text{H}-\text{H}$ bond.

The mechanisms by which the hydrogen reactions proceed offer important clues as to the mechanisms of the hydrocarbon reactions. The hydrocarbons are, like hydrogen, normally in singlet states,* so that reaction on potential-energy surfaces similar to those designated above is possible. However there is an alternative process which is available to the hydrocarbons; this is the ejection of a hydrogen molecule with the formation of a more unsaturated molecule. This process, which frequently occurs with the olefins, is sometimes restricted for energetic reasons, and sometimes by the necessity for

* The evidence for this is to be found in the references quoted later (21-25) in connection with the excited states.

conservation of spin angular-momentum. The conditions under which this reaction can proceed will be discussed in detail later.

REACTION MECHANISMS

The principal reactions that a hydrocarbon can undergo on collision with an excited atom may now be considered. Denoting the excited atom by A^* and the hydrocarbon (saturated or unsaturated) by MH_2 , the two alternative initial steps are:



and

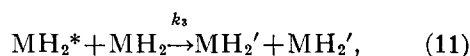
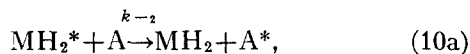


Process (9) is the exact analog of processes (4)–(6), and the potential-energy surfaces upon which reaction takes place are similar in multiplicity to those with hydrogen: if A^* is singlet-excited, the surfaces will be all singlets, while if it is triplet-excited, they will be triplets. From the probable shape of the potential-energy surfaces it can be inferred that reaction (9) will take place without activation energy, provided that the excitational energy of A^* plus the heat of formation of the hydride AH is at least as great as the bond strength $HM-H$. The reactions will, however, proceed with velocities lower than those calculated using collision theory if there are restrictions to crossings between any of the potential-energy surfaces.

In reaction (10) the product formed may in general have excitational energy in the form of electronic, translational, rotational, and vibrational energy. If there is a change of multiplicity in the process $A^* \rightarrow A$ there must be a compensating change from MH_2 to MH_2^* for conservation of spin angular-momentum; this means, for example that, if A^* is in a triplet state and A and MH_2 are in singlet states, MH_2^* must be in a triplet state. It follows that reaction (10) will not occur if there is no sufficiently low electronically-excited state of the right multiplicity, and it seems likely that reaction of this type does not occur between triplet-excited atoms and the saturated hydrocarbons, owing to the lack of a triplet-excited state of sufficiently low energy. When there is no change of multiplicity in the process $A^* \rightarrow A$, the excited molecule MH_2^* is

not required to have electronic excitational energy, and all of its excitational energy can be in the other forms. This situation appears to exist in the reactions of the singlet-excited atoms, but it will be seen that the conversion of a large amount of electronic energy to the other forms proceeds with difficulty.

Reaction (9) is followed by chain processes leading to polymerization; the details will not be discussed here. Reaction (10) may be followed by a number of distinct processes, of which the most important are:



Of the de-activations (10a) and (11), the former is simply the reverse of (10). It is probable that in most cases this reaction will proceed much more slowly than the remaining reactions, since it virtually has an activation energy. Of the energy transferred to MH_2 during reaction (10) some, at least, will be in the form of translational energy, i.e., of heat, so that the reaction will be exothermic. This translational energy, being rapidly dissipated, will have to be reacquired for process (10a) to take place, and this process will therefore proceed slowly and its rate will be temperature-dependent. It should hence be possible to ignore reaction (10a), at any rate at lower temperatures, since the remaining reactions probably proceed without activation energy; this will be done in the treatment which follows.

Reaction (11) represents de-activation by collision with other hydrocarbon molecules. Translational and rotational energy are rapidly dissipated [and therefore play little part in reactions (12) and (13)], excess vibrational energy survives many collisions, while electronic energy is transferred into other forms even more slowly. To show this persistence of electronic and vibrational energy the molecules produced in reaction (11) are marked with a prime (') indicating that they still retain some energy.

Reaction (12) represents the formation of a more unsaturated molecule together with a hy-

drogen molecule. With the olefines such products (i.e., acetylenes) have sometimes been obtained, but in other cases the reaction does not occur. This has been explained² on the basis of energy considerations, due regard being paid to the necessity for conservation of spin angular-momentum. The detachment of a hydrogen molecule from a normal molecule is endothermic, so that, if the acetylene produced is in its lowest state, the condition for reaction is that the excitational energy given to the olefin is at least as great as the endothermicity. If the acetylene is not in its lowest state, its excitational energy must also be taken into account, and it will be seen later that the kinetic results give some tentative limits for the excitational energy of acetylene.

Reaction (13) gives rise to the same products as (9), and will be followed by polymerization processes. From the kinetic results it is not always possible to distinguish experimentally between the direct formation of MH and H [process (9)] and formation *via* the intermediate formation of the complex MH_2^* [process (10) followed by (13)], because the latter reduces to the former as a special case when the rate of de-activation is not important.

The scheme of reactions (9) to (13) is sufficiently general for the purpose of the arguments which follow, but does not cover every possibility. For example, in the case of 1-butene, one reaction which occurs is isomerization to 2-butene; this process will, however, be regarded as a special case of reaction (11).

The rates of the various over-all processes may now be derived in terms of the individual rate constants. The over-all rates that will be expressed are (1) the rate of quenching, (2) the rate of polymerization, and (3) the rate of formation of the molecule M. These rates will be obtained on the basis of steady-state conditions, which will obtain because $[\text{MH}_2^*]$, the concentration of excited molecules, is small, with the result that its rate of change with time is negligible compared with other rates; *viz*:

$$\frac{d[\text{MH}_2^*]}{dt} = 0 = k_2[\text{A}^*][\text{MH}_2] - [\text{MH}_2^*](k_3[\text{MH}_2] + k_4 + k_5), \quad (14)$$

whence

$$[\text{MH}_2^*] = k_2[\text{A}^*][\text{MH}_2] / (k_3[\text{MH}_2] + k_4 + k_5). \quad (15)$$

The rate of quenching is equal to the combined rates of reactions (9) and (10), i.e., to

$$-k[\text{A}^*]/dt = (k_1 + k_2)[\text{A}^*][\text{MH}_2]. \quad (16)$$

This result assumes that a reaction (10a) can be neglected, which has been seen to be usually the case; if reaction (10a) had an appreciable rate, the rate of quenching would be somewhat less than given by Eq. (16).

The rate of formation of the compound M is given by

$$\frac{d[\text{M}]}{dt} = k_4[\text{MH}_2^*] \quad (17)$$

$$= k_4 k_2 [\text{A}^*][\text{MH}_2] / (k_3[\text{MH}_2] + k_4 + k_5), \quad (18)$$

by use of Eq. (15).

The rate of disappearance of MH_2 to form H and the radical MH, is given by

$$-d[\text{MH}_2]_{\text{rad.}}/dt = k_1[\text{A}^*][\text{MH}_2] + k_5[\text{MH}_2^*] \quad (19)$$

$$= k_1[\text{A}^*][\text{MH}_2] + (k_5 k_2 [\text{A}^*][\text{MH}_2] / (k_3[\text{MH}_2] + k_4 + k_5)). \quad (20)$$

If α is the average number of polymer molecules produced by each H atom and MH radical, the rate of polymerization is

$$\frac{k[\text{poly.}]}{dt} = \alpha \{ k_1[\text{A}^*][\text{MH}_2] + (k_5 k_2 [\text{A}^*][\text{MH}_2] / (k_3[\text{MH}_2] + k_4 + k_5)) \}. \quad (21)$$

Actually α is not a constant, and may be pressure-dependent, but no important error should arise from treating it as constant in the arguments which follow.

Equations (16), (18), and (21), which give the rates for the three main processes, indicate rather complex kinetic behavior, and it is possible to distinguish a large number of special cases according to the degree to which certain of the rates are negligible. Fortunately each of the reactions which have been studied seems to fall fairly clearly into one of four different cases, so that a considerable simplification in the kinetic equations is possible in individual instances. The main classification depends upon whether either k_1 or k_2 can be neglected compared with the other, and in all of the reactions one of these conditions is realized. A sub-classification depends upon the relative rates of reactions (11), (12), and (13). The important cases will now be

discussed, and mention will be made of reactions which fall into them; the reactions will later be discussed in detail in terms of the kinetic evidence and certain theoretical considerations.

Case I. If $k_1 \gg k_2$ the rate of quenching will be given by

$$-d[A^*]/dt = k_1[A^*][MH_2], \quad (22)$$

the rate of polymerization will be

$$d[\text{poly.}]/dt = \alpha k_1[A^*][MH_2], \quad (23)$$

while the rate of M-formation will be small. This case arises:

(1) in the reactions of the saturated hydrocarbons, when the rate of process (10) is low, owing to the absence of suitably placed electronically-excited states, and

(2) in the reactions of the singlet-excited atoms with ethylene, owing to the lack of a singlet-excited level of ethylene.

Case II. If $k_2 \gg k_1$ the rate of quenching is given by

$$-d[A^*]/dt = k_2[A^*][MH_2], \quad (24)$$

the rate of polymerization by

$$d[\text{poly.}]/dt = \alpha k_5 k_2 [A][MH_2] / (k_3[MH_2] + k_4 + k_5), \quad (25)$$

and the rate of M-formation by

$$d[M]/dt = k_4 k_2 [A^*][MH_2] / (k_3[MH_2] + k_4 + k_5). \quad (26)$$

Before this case is sub-divided it may be re-

marked, in anticipation of some of the arguments of the following section, that the quenching results in general allow a decision to be made between cases I and II. Under conditions where there are no special restrictions to either of the reactions (9) or (10), as with $Hg(^3P_1)$ and C_2H_4 , it seems that the ratio k_2/k_1 is of the order of 100, which automatically places the reaction in case II or one of its sub-divisions. However in certain instances, when the molecule has no suitable electronic state, k_2 is very low, and case I arises. It therefore follows that case II will be associated with a high quenching rate, and case I with a low one; the two cases may therefore be distinguished on the basis of the quenching data.

The two important subdivisions of case II are as follows.

Case IIa. If in addition to $k_2 \gg k_1$, $k_4 + k_3[MH_2] \gg k_5$, the rate of quenching is still given by Eq. (24), the rate of polymerization will be small, while the rate of M formation is given by

$$d[M]/dt = k_4 k_2 [A^*][MH_2] / (k_3[MH_2] + k_4). \quad (27)$$

This case arises in the reactions of ethylene and butadiene sensitized by $Hg(^3P_1)$.

Case IIb. If in addition to $k_2 \gg k_1$, $k_5 + k_3[MH_2] \gg k_4$, the rate of quenching is given by Eq. (24) (and is high), the rate of polymerization is given by

$$d[\text{poly.}]/dt = \alpha k_5 k_2 [A^*][MH_2] / (k_3[MH_2] + k_5), \quad (28)$$

while the rate of M formation is small. This

TABLE III. Summary of kinetic behavior. MH and H produce on the average α -molecules of polymer.

Case	Conditions	Rate of quenching	Rate of polymerization	Rate of M formation
General	—	$(k_1 + k_2)[A^*][MH_2]$	$\alpha \left\{ k_1[A^*][MH_2] + \frac{k_3[AH_2] + k_4 + k_5}{k_5 k_2 [A^*][MH_2]} \right\}$	$\frac{k_4 k_2 [A^*][MH_2]}{k_3[MH_2] + k_4 + k_5}$
I	$k_1 \gg k_2$	$k_1[A^*][MH_2]$	$\alpha k_1[A^*][MH_2]$	Small
II	$k_2 \gg k_1$	$k_2[A^*][MH_2]$	$\alpha \frac{k_5 k_2 [A^*][MH_2]}{k_3[MH_2] + k_4 + k_5}$	$\frac{k_4 k_2 [A^*][MH_2]}{k_3[MH_2] + k_4 + k_5}$
IIa	$\left\{ \begin{array}{l} k_2 \gg k_1 \\ k_4 + k_3[MH_2] \gg k_5 \end{array} \right\}$	$k_2[A^*][MH_2]$	Small	$\frac{k_3[MH_2] + k_4 + k_5}{k_4 k_2 [A^*][MH_2]}$
IIb	$\left\{ \begin{array}{l} k_2 \gg k_1 \\ k_5 + k_3[MH_2] \gg k_4 \end{array} \right\}$	$k_2[A^*][MH_2]$	$\alpha \frac{k_5 k_2 [A^*][MH_2]}{k_3[MH_2] + k_4 + k_5}$	Small
III	$k_1, k_4, \text{ and } k_5 \text{ small}$	$k_2[A^*][MH_2]$	Small	Small

TABLE IV. Quenching cross sections, and values of $I(A)$ and $I(A) - Ex$.

Quenching gas	Na(3P)	Hg(3P_1)	Cd(3P_1)
	(\AA^2)	(\AA^2)	(\AA^2)
Inert gases	0	0	0
H ₂	7.4 ^a	6.01 ^b	3.45 ^e 0.67 ^f
CH ₄	0.11 ^a	0.059 ^c	0.012 ^e
C ₂ H ₆	0.17 ^a	0.42 ^c	0.02 ^e
C ₂ H ₄	44.0 ^a	48.0 ^d	24.9 ^e
C ₃ H ₈	52.0 ^a	—	29.1 ^e
C ₂ H ₂	—	—	22.0 ^e
Isobutene (C ₄ H ₈)	—	—	30.6 ^e
$I(M) - (\text{kcal.})$	118.0	239.2	206.5
$I(M) - Ex(\text{kcal.})$	69.7	127.2	119.2

^a R. G. W. Norrish and W. M. Smith, Proc. Roy. Soc. **A176** 295 (1940).

^b M. H. Zemansky, Phys. Rev. **36**, 919 (1930).

^c J. R. Bates, Proc. Nat. Acad. Sci. **14**, 849 (1929); J. Am. Chem. Soc. **52**, 3825 (1930); *ibid.* **54**, 569 (1932).

^d E. W. R. Steacie, Can. J. Research **18**, 44 (1940).

^e E. W. R. Steacie and D. J. Le Roy, J. Chem. Phys. **11**, 164 (1943).

^f H. C. Lipson and A. C. G. Mitchell, Phys. Rev. **48**, 625 (1935).

case seems to be realized in the reactions of propylene, isoprene, isobutene, 1-butene and 2-butene photo-sensitized by Hg(3P_1). The higher value of k_5 as compared with k_4 is probably due to the presence of weak C-H bonds in these molecules.

Case III. If k_1 , k_4 , and k_5 are all small, the rate of quenching is given by

$$-d[A^*]/dt = k_2[A^*][MH_2], \quad (29)$$

while the rates of polymerization and M formation will be small. If k_2 had its normal value, this would represent high quenching accompanied by no reaction, all of the excited molecules formed being deactivated. This case occurs in the quenching of sodium by the hydrocarbons, there being insufficient energy for any of the reactions to take place. It also arises in the quenching of Zn(3P_1) and Cd(3P_1) by ethylene; here k_1 and k_5 have their normal (small) values, there being adequate energy, and k_4 is small on energetic grounds on account of the necessity for the production of triplet-excited states.

The quenching data will now be discussed in more detail, followed by a discussion of the individual chemical reactions. The expressions derived in the present section are summarized in Table III.

THE QUENCHING RESULTS

The importance of the quenching results is that they provide information as to the net

rate of the initial reaction steps (9) and (10) [see Eq. (16)] and therefore supplement the information given by the rate of production of products. Unfortunately, owing to experimental difficulties, some of the quenching rates have not been determined. In Table IV the relevant results are given in the form of quenching cross sections, which are the squares of the quenching radii, i.e., the intermolecular separations that have to be assumed on the basis of simple collision theory, and are proportional to the actual rates of the reactions. It has been shown in Part I⁶ that the theory of absolute reaction rates gives an identical equation to collision (kinetic) theory for reactions of this kind, and that the quenching radius corresponds to the intermolecular separation at which a transition to the ionic state takes place.

Owing to the complexity of the potential-energy surfaces it is not possible to interpret these figures in an exactly quantitative fashion, but a rough treatment is useful in indicating the main factors upon which the rates depend. It was pointed out by Magee⁴ (see Part I) that, if it can be assumed (as is approximately true) that in the region of the potential-energy surfaces under consideration the ionic terms in the polar surface are much more important than the non-ionic, the quenching radius is given very approximately by the expression

$$r_e = 330/I(A) - E(MH_2) - Ex \quad \text{Angstrom units,} \quad (30)$$

where $I(A)$ is the ionization potential of the metal A, $E(MH_2)$ is the electron affinity of the quenching molecule MH_2 , and Ex is the energy of excitation of A; these energies are in kcal. The values of $I(A) - Ex$ for the atoms are included in Table IV. If expression (30) were accurate, the cross sections for the three atoms in the table would fall in the order Na > Cd > Hg, since the values of $I(A) - Ex$ lie in the reverse order. The results for sodium and triplet cadmium are in agreement with this, but mercury falls out of line, indicating that the crude theory is inadequate.

The quenching of triplet cadmium by hydrogen is of special interest since, even if the formation of the hydride is assumed, there is not

quite sufficient energy to break the hydrogen-hydrogen bond. The possibility of physical quenching is excluded by the law of spin angular-momentum, so that the only process that can occur involves an activation energy at least as great as the endothermicity of the process, which is 1.0 kcal. At 300°K such an activation energy brings about a decrease in rate by a factor of 0.17. The fact that the quenching cross section is as high as it is (even accepting the lower value given) shows that the activation energy required is hardly more than the endothermicity. In all the other reactions with triplet mercury and cadmium there is sufficient energy to break a bond, so that zero activation energy is to be expected *a fortiori*; with sodium, as has been seen, quenching proceeds by a purely physical mechanism without the breaking of a bond or electronic excitation, and again there is no evidence of an activation energy.

A striking feature of the results quoted in Table IV is that the unsaturated hydrocarbons have quenching cross sections which are very much larger than those of the paraffins. This result is no doubt to be correlated with the kinetic evidence, already referred to, that the paraffins react at an appreciable rate by only one [reaction (9)] of the two possible mechanisms, while the olefins react by (9) and (10). This implies that there are two alternative ionic surfaces in the case of the olefins, of which one is very low and gives a correspondingly high quenching cross section. The lowness of this surface is probably associated with the high electron affinity of the double bond; consequently reaction (10) may be regarded as an interaction between A^* and the double bond, and (9) between A^* and a hydrogen atom. A rough indication of the relative rates of the two reactions in ethylene may be derived as follows on the assumption that reaction (9) proceeds in ethylene at the same rate as in ethane: since ethylene quenches triplet mercury about a hundred times more rapidly than ethane, k_2 for ethane is about 100 times as great as k_1 for ethylene. This result has already been seen to allow a distinction between case I and case II, and will find further application in the following sections.

THE REACTIONS OF THE SATURATED HYDROCARBONS

The reactions of ethane,⁷ propane,⁸ and butane⁹ photo-sensitized by triplet mercury and cadmium have been studied extensively, and the kinetic evidence, which is fully discussed by Steacie,¹ suggests that the initial step is the splitting of a carbon-hydrogen bond with the formation of a hydrogen atom and a radical, which react further to form polymers. There is no evidence that de-activation processes take place, and this fact, together with the fairly low quenching rates, indicates that reaction proceeds solely by mechanism (9), and that reaction (10), and therefore (11) to (13), do not take place: this is case I. The only alternative explanation for the lack of de-activation and of olefin formation would be that reaction (10) occurred and was followed exclusively by (13). This would, however, require the existence of a suitable triplet-excited state: as will be seen, the evidence is that the triplet state is too high to play a part in these reactions. In any case the assumption that reaction (10) is followed exclusively by (13) implies a very small life for the excited complex, which is physically equivalent to postulating that reaction proceeds by (9). It therefore seems correct to explain the kinetics as falling in case I.

Work has not been carried out with the singlet metals, but theory predicts that again reaction would proceed entirely by the free radical mechanism. The evidence for this is that there is no electronically-excited singlet state of low enough energy to be excited by collision.

THE REACTIONS OF THE UNSATURATED HYDROCARBONS

Ethylene and Triplet Mercury

The mercury photo-sensitization of ethylene has been studied by Steacie and Le Roy¹⁰ who found different behavior at 25° and at 300°C. At 25°C the main products of the reaction are

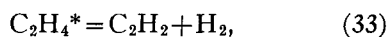
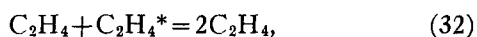
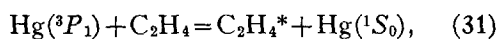
⁷ E. W. R. Steacie and H. W. F. Phillips, *J. Chem. Phys.* **6**, 179 (1938); *Can. J. Research B16*, 303 (1938); E. W. R. Steacie and R. Potvin, *J. Chem. Phys.* **7**, 782 (1939).

⁸ E. W. R. Steacie and D. J. Dewar, *J. Chem. Phys.* **8**, 571 (1940); E. W. R. Steacie, D. J. Le Roy and R. Potvin, *J. Chem. Phys.* **9**, 306 (1941).

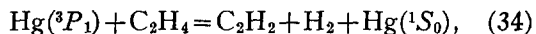
⁹ E. W. R. Steacie and R. Potvin, *J. Chem. Phys.* **7**, 782 (1939).

¹⁰ D. J. Le Roy and E. W. R. Steacie, *J. Chem. Phys.* **9**, 829 (1941); *ibid.* **10**, 676 (1942).

hydrogen, acetylene, butane, and butene. The pressure rises initially and then falls rapidly, the initial pressure rise at low pressures corresponding exactly to the amounts of hydrogen and acetylene produced; at higher pressures, on the other hand, the initial rate of formation of acetylene is greater than the rate of pressure increase. The most significant feature of the low temperature reaction is that the rate decreases with increasing ethylene concentration, indicating a de-activation to be involved, and Steacie and Le Roy suggest the scheme

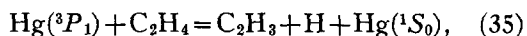


reaction (32) becoming relatively more important as compared with reaction (33) as the pressure is increased. This reaction scheme supersedes that of Taylor and Bates¹¹ who proposed the primary step

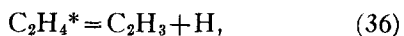


which explains the initial pressure rise but does not account for the decrease of rate with increase of initial pressure.

The formation of butane and butene can be attributed to various reactions. The hydrogen produced in reaction (33) may be photo-sensitized to atoms which will then react with ethylene to form ethyl radicals two of which may combine to form butane. Alternatively, vinyl radicals may be produced by one of the reactions



and



[these correspond to reactions (9) and (13)], and the radicals may react with ethyl radicals to form butene.

As the temperature is increased the rate of the initial pressure rise decreases, becoming zero at 250°C. Moreover, the rate of disappearance of ethylene increases with increase of initial pressure at the higher temperatures, and increases rapidly with increasing temperature.

These facts suggested that at the higher temperatures a free radical mechanism plays a more important part, and this was confirmed by the addition of nitric oxide (which has little effect on the low temperature reaction) which reduced the over-all rate and gave an initial pressure rise at 300°C. At the higher temperatures a good deal of propylene and of compounds of higher molecular weight is formed. The quantum yield for the formation of products other than acetylene and hydrogen was from 5 to 10 times greater at 300°C than at 25°C.

These results may be interpreted in terms of the reaction scheme (9)–(13) as follows. At 25°C the small amount of polymerization suggests that $k_2 \gg k_1$ and that $k_3[\text{C}_2\text{H}_4] + k_4 \gg k_5$; this is therefore an example of case IIa, the rate of acetylene formation being given by

$$\frac{d[\text{C}_2\text{H}_2]}{dt} = k_4 k_2 [\text{Hg}^*] [\text{C}_2\text{H}_4] / (k_3 [\text{C}_2\text{H}_4] + k_4). \quad (37)$$

A crude estimate of the relative importance of k_1 and k_2 at 25°C is 1:100, given by the quenching data.

The question of the increase in rate of the free radical reactions with rise in temperature, and the decrease in importance of the de-activating processes with temperature, will now be discussed in terms of the reaction scheme proposed above [reactions (9) to (13)]. In the general case the rate of olefin formation is given by (18), and the rate of polymerization by (21). The temperature affects the magnitude of these rates by its influence on the rate constants k_1 , k_2 , k_3 , k_4 , and k_5 , the temperature coefficients for which will now be considered.

In order to do this a model for the activated complex has to be assumed in each case. In view of the fact that the quenching rates obey the simple collision theory it seems best to assume that the complexes are held together very loosely, the molecules retaining their individual degrees of freedom; there is, moreover, no evidence of an activation energy for any of the reactions (except (10a), the case of which has been discussed, and which will be ignored). The rate constant for reaction (9) may, on this hypothesis, be expressed as

$$k_1 = (kT/h) F_A F_{\text{MH}} F_{\text{H}} / F_A^* F_{\text{MH}_2}, \quad (38)$$

¹¹ H. S. Taylor and J. R. Bates, J. Am. Chem. Soc. **49**, 2438 (1927).

where the F are the partition functions. Expressing these in terms of their translational, (t), and rotational, (r), parts for each degree of freedom, the equation becomes*

$$k_1 = (kT/h)(t^3)_A(t^3r^3)_{MH}(t^3)_H/(t^3)_A^*(t^3r^3)_{MH_2}. \quad (39)$$

Separating out temperature-dependent parts, gives

$$k_1 = k_1' T (T^{\frac{1}{2}})_A (T^{\frac{1}{2}} T^{\frac{1}{2}})_{MH} (T^{\frac{1}{2}})_H / (T^{\frac{1}{2}})_A^* (T^{\frac{1}{2}} T^{\frac{1}{2}})_{MH_2}, \quad (40)$$

where k_1' is temperature-independent. The equation reduces to

$$k_1 = k_1' T^{5/2}, \quad (41)$$

i.e., the rate constant is proportional to the $5/2$ power of the absolute temperature. It is clear from the derivation that this high temperature-dependence is due to the high entropy of the activated state in which an extra species has been formed.

The rate constant for (10) is given by

$$k_2 = (kT/h) F_A^* F_{MH_2} / F_A F_{MH_2}^*, \quad (42)$$

so that, since the partition function for the activated state has now the same temperature-dependence as that for the initial state, the rate constant is

$$k_2 = k_2' T. \quad (42a)$$

By similar arguments it can be shown that

$$k_3 = k_3' T. \quad (43)$$

The dependence of k_4 on temperature is given by

$$k_4 = (kT/h) F_M F_{H_2} / F_{MH_2} \quad (44)$$

$$= (kT/h) (t^3r^3)_M (t^3r^2)_{H_2} / (t^3r^3)_{MH_2} \quad (45)$$

$$= k_1' T (T^{\frac{1}{2}} T^{\frac{1}{2}})_M (T^{\frac{1}{2}} T)_{H_2} / (T^{\frac{1}{2}} T^{\frac{1}{2}})_{MH_2} \quad (46)$$

$$= k_1' T^{7/2}. \quad (47)$$

Similarly the dependence of k_5 is

$$k_5 = k_5' T^{5/2}. \quad (48)$$

It is thus seen that in spite of there being no activation energy for any of the reactions, some of the rates, namely k_1 , k_4 , and k_5 , show a fairly high temperature-dependence. Since by Eq. (21) the rate of polymerization depends upon k_1

and k_5 , it is clear that this rate will increase significantly between 25°C and 300°C, as was actually found. The rate of acetylene formation, according to Eq. (18), will also increase with temperature owing to the increase in k_4 , but not to the same extent owing to the effect of k_4 in the denominator. Since, moreover, k_4 increases with temperature relative to $k_3[MH_2]$ the importance of de-activations will diminish as the temperature is raised.

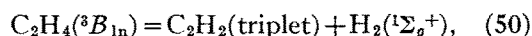
Le Roy and Steacie¹⁰ report that the quantum yield for ethylene disappearance is greater at 300°C than at 25°C by a factor of 5 to 10. According to the scheme of reactions (9) to (13) the rate of ethylene disappearance is given by Eq. (27); the temperature-dependence of the quantum yield therefore depends on those of k_2 , k_3 , and k_4 . Since k_4 varies with the $7/2$ power of the absolute temperature it increases by a factor of about 10 from 25° to 300°C; k_2 and k_3 on the other hand increase by only a factor of 1.9. The theory would therefore predict an increase of quantum yield between these two figures, the higher figure being approached the greater is $k_3[MH_2]$ compared with k_4 .

Ethylene and Triplet Cadmium

The results for the photo-sensitization of ethylene by triplet cadmium atoms¹² differ significantly from those with triplet mercury in that the quantum yield is much lower, being only about 0.015. The high quenching efficiency, on the other hand, indicates that the reaction [reaction (10)]



proceeds at a normal rate, and it therefore appears that the subsequent reactions to give acetylene take place only slowly. This has been interpreted² in terms of the energies involved in the reactions. For conservation of spin angular-momentum the excited ethylene produced in reaction (49) must be in a triplet state, and the acetylene produced by the reaction



must therefore also be in a triplet state. It is estimated that the heat of the reaction analogous

* As an approximation, the vibrational partition functions are assumed to be temperature-independent, and have been omitted.

¹² E. R. R. Steacie and R. Potvin, Can. J. Research **B16**, 337 (1938).

to (50) in which the molecules are in their normal states is about 85 kcal.; hence, if the excitational energies of C_2H_4 (triplet) and C_2H_2 (triplet) are x and y kcal., respectively, the heat of reaction (50) will be about $85 + y - x$ kcal. Since the energy released by the de-activation of the $Cd(^3P_1)$ atom is 87.3 kcal., the energy other than electronic in the triplet-excited C_2H_4 molecule produced in reaction (50) is $87.3 - x$ kcal. If $y > 2.3$ kcal., there will be an activation energy, and reaction will be slow. The slow rate with which the reaction actually proceeds suggests that the latter alternative is the correct one. Since the reaction proceeds readily with triplet mercury it can further be concluded that $y < 27.7$ kcal., this figure being the difference between the excitational energy for triplet mercury, and 87.3.

On the other hand, there is no reason to believe that reactions (9) and (13), involving a bond split, cannot proceed, since the energy released by the $Cd(^3P_1)$ atom (assuming hydride formation) is 102.8 kcal., which is probably greater than the strength of the C-H bond in ethylene (see below). Such reaction as does occur therefore probably proceeds by the free radical mechanism. It is not so easy to predict whether reaction (13) will proceed rapidly, since some of the energy acquired by the excited ethylene will be in the form of translational energy, which will be dissipated rapidly, and enough energy for reaction (13) may not remain. On the assumption that there is not sufficient energy for reaction (13) to proceed, the rate of polymerization will be given by [see Eq. (21)]

$$d[\text{poly.}]/dt = \alpha k_1 [Cd^*][C_2H_4], \quad (51)$$

which will be small since k_1 is normally small; this is an example of case III. Since the quenching rate is given by [see Eq. (16)]

$$-d[Cd^*]/dt = (k_1 + k_2)[Cd^*][C_2H_4], \quad (52)$$

and since k_2/k_1 is large and probably of the order of 100, it follows that unless α is large the quantum yield should be small. The experimental yield is 0.015, and this, together with the rough value of k_2/k_1 , suggests that α is of the order of unity. It is to be noted that the experimental quantum yield is not consistent with the hypothesis that reaction (13) proceeds readily.

In view of the rough numerical agreement this

interpretation of the cadmium reaction seems preferable to that of Steacie,¹ who considers that the low rate is to be attributed to the inhibition of reaction by *both* the free radical and the excited molecule mechanisms.

Ethylene and Triplet Zinc

The results with triplet zinc (13) are very similar to those with cadmium; very little reaction occurs with either. The excitational energy of $Zn(^3P_1)$ is 92.5 kcal., and this suggests that y , the excitational energy of triplet acetylene, is greater than 7.5 ($= 92.5 - 85$) kcal. The results with zinc, therefore, further narrow the limits of the excitational energy of acetylene to 7.5 and 27.7 kcal. The accuracy of these figures is, of course, dependent on the reliability of the figure 85 kcal. for the heat of dissociation of ethylene into acetylene and hydrogen.

Ethylene and Singlet Zinc and Cadmium

The reactions of ethylene photo-sensitized by singlet zinc¹³ and cadmium¹⁴ have also been studied. With cadmium, reaction occurs readily with a quantum yield of about unity, the products being olefines together with small amounts of acetylene and hydrogen. These facts suggest that the reaction proceeds mainly by the free radical mechanism and that the excited molecule mechanism takes place to a small extent only. The reason for the low rate of the excited molecule reaction is not immediately clear; it is not to be explained, as it was with triplet cadmium, in terms of insufficient energy for the formation of acetylene, since there is now ample energy (124.4 kcal.), and the acetylene does not have to be excited electronically as there is no change of multiplicity. This suggests strongly that the low rate of production of acetylene is due to the low rate of reaction (10) itself. The excited ethylene formed in reaction (10) must, for conservation of spin angular-momentum, be in a singlet state, and this must be its lowest electronic state since there is no excited singlet state of ethylene with sufficiently low energy. The excitational energy of the

¹³ H. Habeeb, D. J. Le Roy, and E. W. R. Steacie, *J. Chem. Phys.* **10**, 261 (1942).

¹⁴ E. W. R. Steacie and D. J. Le Roy, *J. Chem. Phys.* **10**, 22 (1942).

ethylene must therefore be entirely in the form of non-electronic energy, and most will be vibrational energy. It therefore appears that the transfer of large amounts of electronic energy into vibrational energy proceeds only slowly.

The reaction, therefore, seems to be an example of case I ($k_1 \gg k_2$). The results with singlet zinc are similar to those with cadmium except that the amount of acetylene produced is even smaller. With zinc more electronic energy has to be converted into vibrational energy, and the rate will be even further reduced on this account. The singlet-mercury reaction has not yet been investigated, but as the electronic energy available is still higher than with zinc (153.9 as compared with 133.4 kcal.), it might be anticipated that the rate of the excited-molecule reaction would be still lower.

It is to be noted that this interpretation of the reactions of the singlet atoms, postulating as it does that the primary reaction which forms the excited molecule proceeds slowly, implies that the quenching rates (which have not been determined) would be low. The mechanism of quenching would in fact be similar to that of the saturated hydrocarbons, and it is to be expected that the cross sections would be of the same order as those found with the saturated hydrocarbons.

Ethylene and Sodium (2P); Strength of the C—H Bond in Ethylene

Ethylene strongly quenches excited sodium (see Table IV) but no reaction occurs; this is presumably because the energy available even with hydride formation (99.9 kcal.) is insufficient to break the carbon-hydrogen bond in ethylene, while the energy that could be given to excite the ethylene (48.3 kcal.) is insufficient for acetylene formation; this is case III. There is considerable doubt about the strength of this C—H bond, and the only directly obtained value, that of 91 kcal. provided by electron-impact data,¹⁵ is almost certainly too small. One piece of evidence for this is derived from the results of J. O. Smith and H. S. Taylor¹⁶ on the reaction between methyl groups and the various hydrocarbons,

¹⁵ D. P. Stevenson, J. Am. Chem. Soc. **64**, 1588 (1942); *ibid.* **65**, 209 (1943).

¹⁶ J. O. Smith and H. S. Taylor, J. Chem. Phys. **7**, 390 (1939); *ibid.* **8**, 543 (1940).

a C—H group in the hydrocarbon being broken with the formation of methane. Since ethylene reacts much less readily than ethane, with an activation energy of at least 2 kcal. higher, it would appear that the C—H bond in ethylene is stronger than that in ethane (97 kcal.) and that its strength is more probably about 100 kcal. This figure is consistent with the failure of excited sodium (99.9 kcal.) to induce reaction (which the figure 91 kcal. would not be) and is also consistent with the results with $\text{Cd}(^3P_1)$; as already seen, it is probable that $\text{Cd}(^3P_1)$ effects reaction readily by the free radical mechanism, and this would impose an upper limit of 102.8 kcal. on the strength of the bond. The kinetic results therefore indicate that the correct value for the strength of the C—H bond in ethylene is approximately 100 kcal.

Butadiene and Triplet Mercury

Butadiene ($\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$) is structurally analogous to ethylene in that its C—H groups are all olefinic, and it is therefore to be expected that its photo-sensitized reactions will be similar. That this is so with triplet mercury has been shown by Gunning and Steacie,¹⁷ who found that the initial rate of polymerization decreases with decreasing pressure. The reaction products were principally a dimer, hydrogen, and an acetylenic compound (C_4H_4). The results are consistent with the hypothesis that the main initial step is the formation of an excited butadiene molecule [reaction (10)] which may either dimerize on collision with another butadiene molecule or split off hydrogen to give C_4H_4 [reaction (12)]. As was the case with ethylene, reaction by way of the free radical [reactions (9) and (13)] seems to be negligible. The quantum yield of the reaction was of the order of unity, indicating that when the excited molecule collides with another molecule de-activation takes place to a minor extent compared with dimerization. This reaction is an example of case IIa.

Propylene and Triplet Mercury

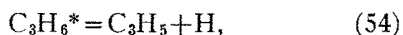
Propylene ($\text{H}_2\text{C}=\text{CH}-\text{CH}_3$) differs from ethylene and butadiene in having three C—H

¹⁷ H. E. Gunning and E. W. R. Steacie, J. Chem. Phys. **12**, 484 (1944); see also D. H. Volman, J. Chem. Phys. **14**, 467 (1946).

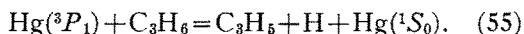
bonds which are once removed from a double bond, and since these are believed to be somewhat weaker than C—H bonds which are next to a double bond, it might be expected that there would be a greater tendency for reaction to proceed by a free radical mechanism. The results of Gunning and Steacie¹⁸ show a low quantum yield and a decrease in rate with increasing pressure, suggesting that de-activations are important and that, therefore, the reaction



where C_3H_6^* is triplet-excited, plays an important part. On the other hand, the main products are liquid polymers and hydrogen, indicating that free radicals are produced by the processes



and



The rate of decomposition of C_3H_6 into $\text{C}_3\text{H}_4 + \text{H}_2$ seems to be small compared with the rates of the above reactions, so that the reaction falls into case IIb ($k_4 \ll k_5 + k_3[\text{C}_3\text{H}_6]$). The greater rates of (54) and (55) as compared with the corresponding ones with ethylene and butadiene are no doubt due to the lower strength of the C—H bond in propylene, evidence for which was given by the free radical investigations of Smith and Taylor.¹⁶

Isoprene and Triplet Mercury

The results for the polymerization of isoprene ($\text{CH}_2=\text{CHC}(\text{CH}_3)=\text{CH}_2$) photo-sensitized by $\text{Hg}(^3P_1)$ ¹⁸ are closely analogous to those of propylene, the quantum yield being low and the rate decreasing with initial pressure.

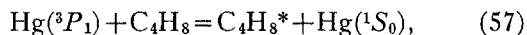
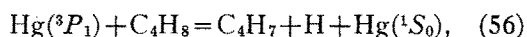
Isobutene and Triplet Mercury

Isobutene ($\text{H}_2\text{C}=\text{C}=(\text{CH}_3)_2$) has six C—H bonds in positions once removed from a double bond, and two which are next to a double bond. The results¹⁹ indicate a quantum yield of 0.59, no initial pressure rise, and, as chief products, propylene, a polymer, acetylene, and propane.

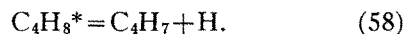
¹⁸ H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **14**, 57 (1946).

¹⁹ H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **14**, 544 (1946).

The products are believed to be formed from H and the radical C_4H_7 , formed by the three processes:



and



As with ethylene and triplet cadmium, the C_4H_8^* does not split off a hydrogen molecule, presumably for energetic reasons, but will be deactivated by collisions. The low quantum yield is due to these de-activations. This is an example of case IIb.

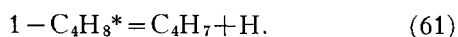
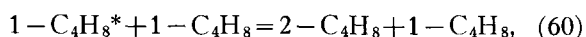
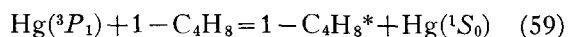
Gunning and Steacie offer an alternative explanation of these results, postulating an inefficiency in the primary process and explaining the low quantum yield in terms of physical quenching in which electronic energy is transferred into vibrational and rotational energy only. However this latter suggestion is not to be maintained, owing to the change of multiplicity which would make such a reaction exceedingly inefficient. The isobutene formed in reaction (57) must be in a triplet-excited electronic state, and only the extra energy set free can pass into vibrational and rotational energy. This type of energy transfer can, of course, be described as physical in this instance, in which it does not lead to chemical reaction, but it must be noted that this kind of quenching does frequently lead to reaction and in favorable cases (as with ethylene and triplet mercury) to very rapid reaction with high quantum yield. The reason for the low rate of decomposition of triplet-excited isobutene cannot be interpreted quantitatively since the energies are not known, but it is doubtless associated with the energies of the triplet-excited molecules that have to be formed in subsequent reactions.

1-Butene and Triplet Mercury

The products formed in the mercury-photo-sensitized reaction of 1-butene ($\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_3$) are chiefly 2-butene and a polymer.²⁰ It is found that increasing the pressure increases

²⁰ D. J. Le Roy and E. W. R. Steacie, *J. Chem. Phys.* **10**, 683 (1942); H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **14**, 581 (1946).

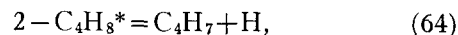
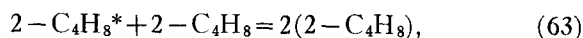
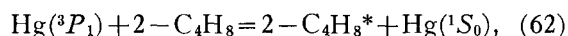
the rate of isomerization but decreases the rate of polymerization. This indicates that isomerization depends upon collisions between excited 1-butene molecules and normal molecules, and that polymerization involves the splitting-off of a hydrogen atom from an excited 1-butene molecule followed by chain processes. The only plausible mechanism would seem to be that proposed by Gunning and Steacie as follows:



This reaction scheme corresponds to our case IIb. The process is of interest in that it was the first to give concrete evidence that free radicals may be produced through an excited molecule having a finite life. On the basis of their kinetic results, Gunning and Steacie conclude that de-activation without isomerization takes place to an insignificant extent compared with (60).

2-Butene and Triplet Mercury

The reaction between 2-butene ($\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}_3$) and triplet mercury²⁰ gives rise mainly to liquid polymer. Except that there is no isomerization the kinetics are similar to those with 1-butene and the scheme



is postulated. This falls into case IIb, and we again have positive evidence that free radicals are formed from C_4H_8^* .

GENERAL DISCUSSION

In spite of the kinetic complexity of the photo-sensitized reactions of the hydrocarbons, it has been possible to classify them into four groups. There is naturally some variation within one group, but this seems to be considerably less important than the variations between reactions lying in different groups.

The classification which has been made depends upon the following assumptions which the analysis of the kinetic results seems to make necessary:

1. When there is a suitable electronic state to absorb part of the energy of excitation, the rate of formation of the excited hydrocarbon [reaction (10)] occurs with about one hundred times the velocity with which the C-H bond is broken [reaction (9)]. This is case II.
2. When there is no suitable electronic state of the hydrocarbon molecule, the rate of formation of the excited hydrocarbon, which must have its excitational energy in the form of vibrational and rotational energy, must be very low (case I).
3. When all of the C-H bonds in the hydrocarbon are next to a double bond, the excited hydrocarbon readily splits off a hydrogen molecule (case IIa).

TABLE V. Summary of conclusions.

Hydrocarbon	Sensitizer	Case	Conditions	Remarks
Ethane } Propane } Butane }	$\{\text{Cd}(^3P_1)\}$ $\{\text{Hg}(^3P_1)\}$	I	$k_1 \gg k_2$	No triplet-excited states
Ethylene	$\text{Zn}(^3P_1)$	III	k_1, k_2, k_4, k_5 small	Insufficient energy
Ethylene	$\text{Cd}(^3P_1)$	III	k_1, k_2, k_4, k_5 small	Insufficient energy
Ethylene	$\text{Hg}(^3P_1)$	IIa	$k_2 \gg k_1, k_4 + k_3[\text{C}_2\text{H}_4] \gg k_5$	Triplet-excited state
Ethylene	$\text{Zn}(^1P_1)$	I	$k_1 \gg k_2$	No singlet-excited states
Ethylene	$\text{Cd}(^1P_1)$	I	$k_1 \gg k_2$	No singlet-excited states
Ethylene	$\text{Na}(^2P)$	III	k_1, k_4, k_5 small	Insufficient energy
Butadiene	$\text{Hg}(^3P_1)$	IIa	$k_2 \gg k_1, k_4 + k_3[\text{C}_4\text{H}_6] \gg k_5$	Triplet-excited state { Low energy C-H bonds favoring (5) as compared with (4) }
Propylene	$\text{Hg}(^3P_1)$	IIb	$k_2 \gg k_1, k_5 + k_3[\text{C}_2\text{H}_6] \gg k_4$	
Isoprene	$\text{Hg}(^3P_1)$	IIb	$k_2 \gg k_1, k_5 + k_3[\text{C}_2\text{H}_6] \gg k_4$	
Isobutene	$\text{Hg}(^3P_1)$	IIb	$k_2 \gg k_1, k_5 + k_3[\text{C}_2\text{H}_6] \gg k_4$	
1-Butene	$\text{Hg}(^3P_1)$	IIb	$k_2 \gg k_1, k_5 + k_3[\text{C}_2\text{H}_6] \gg k_4$	
2-Butene	$\text{Hg}(^3P_1)$	IIb	$k_2 \gg k_1, k_5 + k_3[\text{C}_2\text{H}_6] \gg k_4$	

4. When the molecule has C—H bonds which are next but one to a double bond, and which are consequently weak, the excited molecule may split off a hydrogen atom to the exclusion of a hydrogen molecule (case IIb).

5. Sometimes, when the exciting atom has insufficient energy, the excited molecule produced may be unable to perform any reaction (case III).

The allocation of the reactions to the various groups is summarized in Table V.

Since the arguments of the present paper are concerned with the existence or non-existence of electronically-excited states of the hydrocarbons, consideration will be given to the question of what other and more direct evidence is available.

The simple saturated hydrocarbons do not absorb except at very low wave-lengths, and therefore have no low-lying singlet energy levels. Mulliken²¹ estimates the excitational energy of the lowest singlet (1T_2) state of methane to be about 225 kcal. The lowest excited triplet state (3T_2) of methane should be lower, but Mulliken estimates its energy as at least 140 kcal. The excitation energies of both singlet and triplet states are thus too high for the states to be produced in any of the reactions discussed here, and this is consistent with the observed quenching and kinetic data.

The singlet-excited states of the olefins are also very high. Absorption starts with ethylene at about $57,000\text{ cm}^{-1}$ which corresponds to about 160 kcal.²² In the case of sodium and the singlet atoms there is, therefore, not enough energy for electronic excitation, and the excitational energy must all be taken up as vibrational energy. As

has been seen, the evidence suggest that this transfer of energy takes place more readily the smaller the amount of energy that has to be transferred. Thus excited sodium, which has only a small amount of energy (48.3 kcal.), is strongly quenched by the unsaturated hydrocarbons. Unfortunately the quenching rates with the singlet atoms are not known; however, singlet cadmium, which has 124.4 kcal. of energy to transfer, produces only small amounts of acetylene and hydrogen from ethylene, while singlet zinc, with 133.4 kcal. produces even less. It is difficult to see how these results would be explained except on the basis given.

The energy of the triplet state of the olefins has been a matter of considerable discussion. On qualitative grounds a fairly low lying state is to be expected, corresponding to the uncoupling of one of the electron pairs in the double bond (compare oxygen). Magee, Shand, and Eyring²³ have postulated that the excitational energy is about 20 kcal., on the basis of an activation energy of this value for certain isomerizations involving rotation about the double bond. However, Hartmann²⁴ has calculated the energy to be 70 kcal., in good agreement with the value of 72–74 kcal. obtained by G. N. Lewis and M. Kasha²⁵ on the basis of their phosphorescence studies. In any case the energy appears to be sufficiently low to allow the formation of a triplet-excited state in the case of all of the reactions with the triplet atoms.

²¹ R. S. Mulliken, *J. Chem. Phys.* **3**, 517 (1935).

²² W. C. Price and W. T. Tutte, *Proc. Roy. Soc. A* **174**, 207 (1940).

²³ J. L. Magee, W. Shand, and H. Eyring, *J. Am. Chem. Soc.* **63**, 2100 (1944).

²⁴ H. Hartmann, *Zeits. physik. Chemie* **B53**, 96 (1943).

²⁵ G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **66**, 2100 (1944).