

## GENERAL DISCUSSION.

**Dr. H. Steiner** (*Manchester*) said: With reference to Prof. Hinshelwood's questions regarding the low steric factors of reactions of hydrogen atoms and also of methyl radicals with hydrocarbons, may I put forward a suggestion, which, though probably not applicable to the reactions of methyl radicals, may be of importance in the case of the hydrogen atom reactions. Some years ago Prof. Rideal and I, when investigating exchange reactions of deuterium and hydrogen chloride<sup>1</sup> were led to study the transition complex  $\text{H} \cdots \text{Cl} \cdots \text{H}$  using the semi-empirical method of Eyring,<sup>2</sup> this complex being typical of exchange reactions of the type,

<sup>1</sup> Steiner and Rideal, *Proc. Roy. Soc. A*, 1939, **173**, 503.

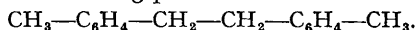
<sup>2</sup> For references, see Glasstone, Laidler and Eyring, *The Theory of Rate Processes* (McGraw-Hill, 1941).

$D + ClH \rightarrow DCl + H$ . We found that the transition complex had considerable stability and should be formed readily because of a low activation energy associated with its formation. Yet experimentally it was found that this reaction does not occur. It is likely that this is due to a very low "transmission coefficient", the deuterium atom instead of reacting being reflected back. Applying to the potential-energy diagrams the rolling-ball picture of Petzer and Wigner,<sup>2</sup> one finds that because of the disparity of masses between the attacking deuterium atom and the central chlorine atom in the complex the energy of reaction cannot be dissipated but remains concentrated as vibrational energy of the newly-formed D—Cl link. As a consequence the D atom splits off again and no reaction occurs. In the reactions studied by Melville and Robb<sup>3</sup> particularly, a similar disparity of masses exists between the attacking hydrogen atom and the carbon atom of the olefine, with which it is to form a link. It may be that for this reason it is difficult to transmit the energy in the newly-formed link and as a result the probability of stabilising the corresponding molecular complex is small. This effect should manifest itself as a low steric factor for these particular reactions.

**Dr. J. Weiss** (*Newcastle*) said: Prof. Hinshelwood has referred in his remarks to the important question of the two possible ways in which free radicals can interact, i.e. dimerisation and disproportionation. It is, of course, not possible to make any definite predictions regarding the behaviour of radicals although it is perhaps possible to outline a few general considerations.

Dimerisation is generally favoured in solution where a third body is practically always present. In the case of radicals with a dipole moment, as for instance OH, dimerisation of the radicals to form  $H_2O_2$  is disfavoured as in this case the negatively-charged ends of the dipoles would have to approach each other to a distance where the valence forces come into play. In general, dipole radicals will tend to assume the position of lowest potential energy, i.e.  $\begin{smallmatrix} + \\ \text{---} \\ - \end{smallmatrix} \begin{smallmatrix} + \\ \text{---} \\ + \end{smallmatrix}$  which, obviously, favours disproportionation. Therefore, in all these cases if disproportionation is possible it will be favoured rather than dimerisation, which is in agreement with experiments.<sup>4</sup>

**Dr. M. Szwarc** (*Manchester*) said: The recombination of atoms is known to be a three-body collision or a wall reaction. It is assumed, however, that the recombination of two radicals can occur as a two-body collision if there are enough degrees of freedom among which the energy released in the association process can be dissipated. The kinetics of the pyrolysis of benzyl iodide, investigated by C. Horrex and myself, seems to indicate that the recombination of benzyl radicals is not an efficient process, and it is quite probable that it requires a third body. Even more clear evidence has been obtained by myself in the study of the *p*-xylyl radicals. These radicals were shown to disproportionate in the gas phase under a pressure of a few mm. Hg, no dimerisation was observed. However, in the liquid phase, where these radicals were produced by the thermal decomposition of acetyl peroxide in *p*-xylene as a solvent, the bulk of resulting product was found to be the dimer,



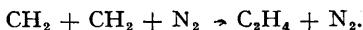
We can conclude, therefore, that the two-body recombination of *p*-xylyl radicals is a rare event, but in the liquid phase where each collision is probably a three-body collision, the dimerisation occurs quite easily.

It seems that we can generalise these observations and state that the recombination of even complex radicals proceeds usually by the three-body mechanism, and the two-body recombination has an extremely small probability factor.

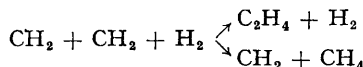
<sup>3</sup> Melville and Robb, this Discussion, p. 131.

<sup>4</sup> Cf. also Weiss, *Trans. Faraday Soc.*, 1940, **34**, 856.

It seems that the results obtained by Bawn and Tipper in their investigation of  $\text{CH}_2$  radicals can be interpreted as an interesting case of a three-body collision leading to two different products of reaction. The recombination of  $\text{CH}_2$  radicals in  $\text{N}_2$  is a three-body reaction :



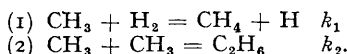
The same reaction in  $\text{H}_2$  can lead to a recombination of either pair of reactors :



If this is the case, then the  $\text{C}_2\text{H}_4/\text{CH}_4$  ratio is independent of  $\text{H}_2$  pressure, and this was actually stated by the authors.

**Dr. C. F. H. Tipper** (*Bristol*) (*communicated*) : In connection with the paper by Steacie, Darwent and Trost, information on the steric factor of the reaction between methyl radicals and hydrogen can be obtained from a calculation using the results of Bawn and Tipper.<sup>5</sup>

It is thought probable that when sodium is passed into excess methyl iodide in hydrogen the methyl radicals formed disappear by the two reactions,



Then

$$\frac{d[\text{CH}_4]}{dt} = k_1[\text{CH}_3][\text{H}_2]$$

$$\frac{d[\text{C}_2\text{H}_6]}{dt} = k_2[\text{CH}_3]^2.$$

Using the usual expression for  $k$ ,  $k = PZe^{-E/RT}$  where  $P$  is the steric factor,

$$\frac{d[\text{CH}_4]}{dt} = P_1 Z_1 e^{-E_1/RT} [\text{CH}_3][\text{H}_2]$$

$$\frac{d[\text{C}_2\text{H}_6]}{dt} = P_2 Z_2 e^{-E_2/RT} [\text{CH}_3]^2$$

dividing

$$\frac{[\text{CH}_4]}{[\text{C}_2\text{H}_6]} = \frac{P_1}{P_2} \cdot \frac{Z_1}{Z_2} e^{-(E_1-E_2)/RT} \frac{[\text{H}_2]}{[\text{CH}_3]}.$$

From experiments at a hydrogen pressure of 5.8 mm. and a temperature of 363° C. the ratio  $\text{CH}_4/\text{C}_2\text{H}_6 = 3.7$ .  $E_1 - E_2$  has been found to be about 9000 cal., and  $Z_1$  can be taken as equal to  $Z_2$ .

The value of the stationary concentration of methyl radicals is somewhat uncertain, but a maximum value is about  $10^{-2}$  mm. (sodium atom pressure). Inserting these values,  $P_1/P_2$  is found to be about 2. If a lower value of  $\text{CH}_3$  of  $10^{-3}$  is taken,  $P_1/P_2$  is 0.2. The values of  $P_1$  and  $P_2$  therefore appear to be of the same order of magnitude.  $P_2$ , the steric factor in the recombination of methyl radicals, is generally considered to be small<sup>6</sup> ( $\sim 10^{-4}$ ) and thus the steric factor for the reaction of the radicals and hydrogen would seem to be small also.

**Dr. H. Steiner** (*Manchester*) said : It has been shown in this Discussion, particularly by Steacie,<sup>7</sup> that considerable differences exist in the reactivities of hydrogen atoms and of methyl radicals with the lower molecular weight hydrocarbons of the paraffin series. The opinion was expressed<sup>8</sup> that this is due mainly to differences in the reactivities of hydrogen atoms bound to carbon by primary, secondary and tertiary bonds respectively. This in turn can be correlated with the corresponding differences in the bond energies of these linkages as was revealed particularly by the later

<sup>5</sup> Bawn and Tipper, *Trans. Faraday Soc.*, this Discussion, p. 103.

<sup>6</sup> Bawn, *Trans. Faraday Soc.*, 1935, **31**, 1536.

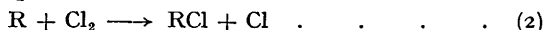
<sup>7</sup> Steacie, Darwent and Trost, this Discussion.

<sup>8</sup> Smith and Taylor, *J. Chem. Physics*, 1939, **7**, 390.

work of Polanyi and collaborators.<sup>9</sup> I wish to report some calculations which Dr. Watson and myself have carried out based on experiments on chlorination of paraffins by Hass and collaborators.<sup>10</sup> The results further illustrate the variations in reactivities of primary, secondary and tertiary carbon-hydrogen bonds. The thermal chlorination of gaseous paraffins at temperatures of 200°-400° c. proceeds by a chain mechanism and it can be shown that the rate-determining step is the reaction of a chlorine atom with the hydrocarbon according to



This is followed by the rapid reaction



leading to the final substitution product.

In the case where reaction with hydrogen atoms on different positions of the same hydrocarbon molecule can take place one obtains different products, the ratio of which directly gives the ratio of the relative rates of reaction (1). Thus in the case of propane we obtain the monochlorination products 1- and 2-chloropropane respectively and the ratio of the yields of the two products directly gives the ratio of the rate of the reaction of a Cl atom with a primary or secondary hydrogen of propane. Whilst by this method it is impossible to obtain absolute reaction rates, the relative rates can be obtained with considerable accuracy. In some cases relative yields have been measured over a range of temperatures and it is then possible to obtain the differences of activation energies and temperature-independent factors separately. In the case of propane we find for the relative reactions of a chlorine atom with a primary and a secondary hydrogen respectively a difference of 1.3 kcal. in the activation energies, while the temperature-independent factors are very nearly equal. In the case of *isobutane* we find a difference of 1.7 kcal. in the activation energies for reaction with the primary and tertiary hydrogen atom respectively; again the temperature-independent factors are equal within the accuracy of the experiments. Assuming that for other hydrocarbons the ratios of the temperature-independent factors are in the same way approximately unity, we can also calculate the activation energy differences in cases where experiments were carried out at one temperature only. In this way, we obtain the following data:

<i>n</i> -butane	$\Delta E_1^2 = 1.3$ kcal./mole.
<i>n</i> -pentane	$\Delta E_1^2 = 1.1$ ,,
<i>isopentane</i>	$\Delta E_1^2 = 1.1$ ,,
<i>isopentane</i>	$\Delta E_1^3 = 1.7$ ,,

where  $\Delta E_1^2$  and  $\Delta E_1^3$  stand for the differences in activation energies of reaction with a primary and secondary, and with a primary and tertiary hydrogen respectively.

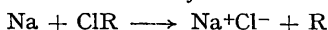
Generally it is seen that there is a difference of 1.1-1.3 kcal. for reaction with a primary and secondary hydrogen respectively, and a difference of 1.7 kcal. for reaction with a primary and tertiary hydrogen. These differences are large if compared with the absolute activation energies of these reactions, which though not well known are of the order of 8-10 kcal., but they are smaller than the differences in bond strength of these bonds as given by Baughan, Evans and Polanyi.<sup>9, 11</sup> These authors find a difference of 6 kcal. in the bond strength of the primary and secondary C—H bond in propane, and if it be assumed that the bond strength of the primary bonds in butane and *isobutane* are approximately equal, one obtains a difference of 8 kcal. in the bond strength of primary and tertiary bonds in *isobutane*.

<sup>9</sup> Baughan, Evans and Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 377.

<sup>10</sup> Hass, McBee and Weber, *Ind. Eng. Chem.*, 1936, **28**, 333.

<sup>11</sup> Butler and Polanyi, *Trans. Faraday Soc.*, 1943, **39**, 19.

For reactions of Na atoms with alkyl halides of the type :



Butler and Polanyi<sup>10</sup> found for a whole series of hydrocarbon radicals R an approximately linear relation between bond strength and activation energy of the type

$$\Delta E = \alpha \Delta H$$

where

$\Delta E$  = difference of activation energy ;

$\Delta H$  = difference of bond strength ;

and  $\alpha$  = constant.  $\alpha$  was shown theoretically to have a value of about 0.3 and experimentally a value of 0.27 was found. It is of interest to apply this relation to the present results where data are available. One finds that in the case of propane  $\alpha = 0.22$  and in the case of *isobutane*  $\alpha = 0.21$ . Thus the same relation seems to hold for these reactions though with a slightly lower proportionality constant. It must be noted that this is by no means to be expected since Polanyi's relation was derived under the assumption that little resonance occurs in the transition state, an assumption which is justified in the particular case of the sodium-flame reaction to which this relation was applied. In contrast to this, resonance should be expected to play an important part in lowering the energy level of the transition complexes of the present reaction, yet the proportionality between bond strength and activation energy still seems to hold with only a slightly lower proportionality constant. This result indicates that differences in the resonance energies of the transition complexes of a chlorine atom reacting with a primary, secondary or tertiary hydrogen respectively of a hydrogen carbon molecule either are non-existent or small enough to be neglected.

**Dr. E. W. R. Steacie** (*Ottawa*) said : The results given in Norrish and Porter's paper give quite a different view of the reactivity of methylene, and are thus quite important. The surprising thing is the number of ways in which they differ from previous work ; a different life-time, lack of specificity of certain mirrors, inefficiency of lead mirrors with acetone, and a virtually bimolecular disappearance of radicals.

The light source was very powerful, and formally one could explain the difference if  $\text{CH}_2$  was not removed by a wall reaction, but by a second-order gas reaction, the rate thus increasing with increasing methylene concentration. This would also explain the second-order nature of the loss of activity. However, it seems unlikely that the concentration here was higher than that in experiments in which methylene was produced by the *thermal* decomposition of ketene.

**Dr. C. H. Bamford** (*Maidenhead*) said : It is difficult to draw any conclusions about radical reactivities from measurements of half-lives unless the precise nature of the radical-destroying reactions are known. Norrish and Porter remark that " the reactions of methyl and methylene radicals with themselves occur with similar readiness under the same conditions." As a conclusion about the reactivities of the radicals this does not seem to be justifiable unless it can be shown that in Norrish and Porter's experiments both radicals disappear in homogeneous reactions. If wall processes are important, the observed rate of reaction will depend not only on the reactivity of the radicals, but also on their accommodation coefficients, and the accommodation coefficients of the carrier gases.

Hitherto it has been agreed that in experiments of this kind at room temperatures the radicals react mainly on the walls. Thus Paneth, Hofeditz and Wunsch<sup>12</sup> showed that heating the tube increases the life of free methyl, and attributed this to a reduction in the accommodation coefficient at high temperatures. Pearson, Purcell and Singh<sup>13</sup> concluded that methylene in diazomethane reacts with the latter on the walls.

<sup>12</sup> Paneth, Hofeditz and Wunsch, *J. Chem. Soc.*, 1935, 372.

<sup>13</sup> Pearson, Purcell and Singh, *ibid.*, 1938, 409.

Norrish and Porter's results at the higher light intensities given on page 98 do not allow of a definite choice between first- and second-order kinetics. The results for  $\text{CH}_2$  taken as a whole give a better first-order plot. (The second-order plot is fairly satisfactory except for the 90 and 95 cm. points, which are a long way out.) Their experiments at lower intensities (Fig. 1 of their paper) give a good second-order plot. The results of Paneth (for  $\text{CH}_3$ ) referred to above show an interesting similarity: for short distances (high concentrations) the order is nearly one, while for long distances it is almost two. These variations would seem to indicate that at high concentrations the radicals react by a first-order process, and at lower concentrations by a second-order process, and thus imply a wall reaction. The experimental indications are therefore that the termination reaction is complex in nature, and it is doubtful if the present technique is capable of providing clear-cut evidence as to the comparative reactivities of the radicals.

**Mr. G. Porter** (*Cambridge*) said: The differences in life-time and reaction-order mentioned by Dr. Steacie are not so surprising if we assume the following.

(a) The recombination of radicals in flow experiments occurs almost exclusively by the collision of a radical from the gas phase with one adsorbed on the wall.

(b) The concentration of radicals adsorbed on the walls is proportional to the pressure of radicals in the gas phase at low concentrations, the total gas pressure being kept constant, but reaches a saturation limit at higher concentrations.

Thus, at high partial pressures the reaction will follow a first-order law, but at low pressures the concentration adsorbed on the walls will be proportional to the partial pressure of radicals in the gas phase and the reaction will change over to a second-order mechanism. The figure of about  $5 \times 10^{-8}$  sec. quoted by several workers for the half life-time of various radicals probably corresponds to the saturation part of the curve and is accompanied by a unimolecular law. From a comparison of concentration measurements, mirror-removal times and kinetics, it appears that the concentration of radicals in our experiments was not very high, despite the powerful lamp; this is quite probable as a relatively small area of the tube was illuminated and the lamp was an inefficient radiator in the region below 3000 Å.\*

These assumptions allow a fairly good description of the experimental data. As Bamford has pertinently pointed out, the kinetics of  $\text{CH}_2$ -removal change from 1st to 2nd order as the concentration in our experiments decreases. The removal of  $\text{CH}_3$  also becomes bimolecular at lower concentrations. Similarly the failure of the unimolecular rate law found by Paneth<sup>14</sup> was accompanied by relatively low radical concentrations, though Paneth inclined to the idea that the reaction was always bimolecular and that the failure to notice departure from linearity was due to "shorter range of measurement and the strong scattering of individual points in the former work". Unfortunately no comparison with high concentration of methylene, obtained by *thermal* decomposition of ketene is possible as this reaction does not appear to produce methylene.<sup>15</sup>

The difference in specificity of metal mirrors is almost certainly due to mirror poisoning and different surface conditions, although we found that bismuth gave particularly reproducible results, and was as reliable as tellurium.

\* In high-pressure mercury lamps of this type, the energy distribution is shifted towards the visible region. In addition, reversal of the 2536 Å. line is complete and the absorption spreads over a considerable portion of the ultra-violet region.

<sup>14</sup> Paneth, Holfeditz and Wunsch, *J. Chem. Soc.*, 1935, 372.

<sup>15</sup> Pearson, Purcell and Saigh, *ibid.*, 1938, 409.

The comparison of radical reactivities on the basis of mirror experiments made by Pearson, ourselves and others does, as Dr. Bamford points out, depend on the assumption that the accommodation coefficients of the radicals compared is the same. It is, however, extremely improbable that under the varied conditions of our experiments the accommodation-coefficient differences should always compensate for the different reactivities of the radicals, nor is there any reason to suppose a vast difference in accommodation coefficients between  $\text{CH}_2$  and  $\text{CH}_3$ , so that, as a test between free-radical or relatively stable molecular behaviour, we believe that the method is valuable. Any more quantitative interpretation of the results of mirror experiments, especially comparisons under different conditions of concentration and surface, must be accepted with reserve.

**Dr. G. A. McDowell** (*Liverpool*) (*communicated*): Norrish and Porter in discussing the structure of methylene state that "in the singlet state we are dealing with bonds arising from a pure  $p$  carbon atomic orbital, whereas the bonds in the triplet structure can be  $sp$  diagonal hybrids"; and as this seems to be a common belief it is perhaps necessary to point out that Mulliken<sup>16</sup> and Lennard-Jones<sup>17</sup> have shown by the methods of group theory that it is possible for the bonds in the singlet state of methylene also to be  $sp$  hybrids. The group theoretical treatment of this problem is very simple and goes along the following lines. The carbon atom, in its ground state, has one  $2s$ , and three  $2p$  atomic orbitals available for bond formation, and the hydrogen atom has, of course, only a

TABLE I.—CHARACTER TABLE FOR SYMMETRY GROUP  $C_{2v}$ .

		$E$ .	$C_2$ .	$\sigma_v$ .	$\sigma_v'$ .
$A_1$	.	I	I	I	I
$A_2$	.	I	I	—I	—I
$B_1$	.	I	—I	I	—I
$B_2$	.	I	—I	—I	I

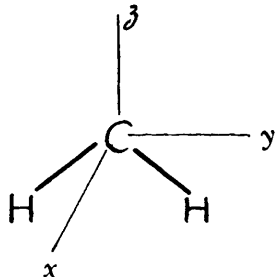


FIG. 1(a).—Methylene with symmetry  $C_{2v}$ .

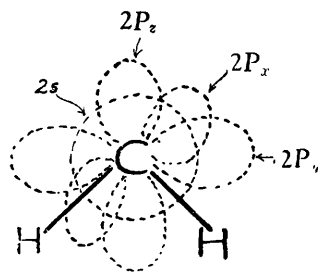


FIG. 1(b).—Showing the  $2s$ ,  $2p_x$ ,  $2p_y$ ,  $2p_z$ , atomic orbitals of the C atom.

$1s$  orbital. When methylene is formed the orbitals available for bond formation are determined by the symmetry of this compound. There are only two possible structures for methylene (a) angular symmetric belonging to point group  $C_{2v}$ ; (b) linear symmetric belonging to point group  $D_{\infty h}$ . The angular symmetric form ( $C_{2v}$ ) gives rise to the singlet state. The character table for group  $C_{2v}$  is shown above (Table I). Suppose we choose our co-ordinates as shown in Fig. 1(a) and then inquire how the  $2s$ ,  $2p_x$ ,  $2p_y$ ,  $2p_z$ , atomic orbitals of the carbon atom behave under the operations of this group, i.e. we determine to which irreducible representation the various orbitals belong. This is important for it can be

<sup>16</sup> Mulliken, *Physic. Rev.*, 1932, 41, 751.

<sup>17</sup> Lennard-Jones, *Trans. Faraday Soc.*, 1934, 30, 70.



shown that when a bond is formed hybridisation can only occur between orbitals belonging to the same irreducible representation of the symmetry group of the resulting molecule.

The  $2s$  orbital of the carbon atom is spherically symmetrical and so obviously belongs to representation  $A_1$ . We shall represent the symmetry of the molecular orbital by small letters, hence we say that this orbital has symmetry  $a_1$ . Of the three  $2p$  atomic orbitals of the carbon atom it is easily seen that they have the following symmetries,  $2p_z \sim b_1$ ,  $2p_y \sim b_2$ ,  $2p_x \sim a_1$ . Since the  $2s$  and  $2p_x$  orbitals belong to the same representation,  $a_1$ , hybridisation is possible when methylene with symmetry  $C_{2v}$  is formed, i.e. in the  $^1A_1$  or singlet state.

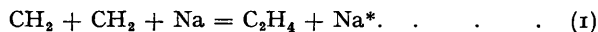
The operations of rotation and reflection of this group turn one hydrogen atom into the other; and it is, therefore, necessary to take linear combinations of these two hydrogen orbitals. It can be shown by forming the direct products  $\sum_i X_i(R)R\phi$  that the proper combinations are  $H_A = H_B$ .

The former belongs to class  $a_1$  while the latter belongs to class  $b_2$ . The  $a_1$  orbitals are of two types which we shall call  $(a_1)_1$  and  $(a_1)_2$ . Hence the following molecular orbitals are possible when methylene in the  $A_1$  state is formed:—

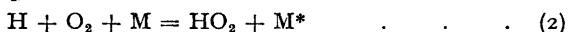
$$\begin{aligned}(a_1)_1 &= a(2s) + b(H_A + H_B) = c(2p_z) \\ (b_2) &= d(2p_y) + e(H_A - H_B) \\ (a_1)_2 &= f(2p_x) + g(H_A + H_B) + h(2s).\end{aligned}$$

According to Mulliken and Lennard-Jones the C—H binding is governed by all three orbitals.

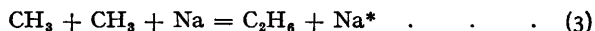
**Dr. A. D. Walsh** (*Cambridge*) (*communicated*): It is clearly of the utmost importance to be sure of the origin of the sodium excitation energy in the experiments of Bawn and his collaborators: for the interpretation given by Bawn has a direct bearing on the structure of the methylene radical. Can we completely rule out the possibility that this excitation energy comes from the recombination of  $CH_2$  radicals to give  $C_2H_4$ ?



The energy available is of course ample. Moreover, we need not suppose a triple collision (which has the objections already pointed out by Bawn and Dunning<sup>18</sup>) in the simplest sense. If two  $CH_2$  radicals combine, the resulting  $C_2H_4$  (even though excessively energy-rich) may have an appreciable life simply through some of its energy of formation passing into vibrational degrees of freedom and an appreciable time may elapse before the molecule again assumes the phase in which all the energy is available for decomposition. Minkoff<sup>19</sup> has described a similar process in the formation of energy-rich  $HO_2$ , so that the reaction



commonly accepted as occurring in the  $H_2-O_2$  reaction, need not involve a triple collision in the ordinary sense. Certainly, if energy-rich  $C_2H_4$  is formed, it seems plausible that it should be capable of transferring energy to a sodium atom on collision for it has been shown<sup>20</sup> that the reverse process occurs readily. Evidently the relevant potential-energy surfaces are such that crossing is quite possible. On the other hand, the comparatively small radius of cross-section found for the quenching by  $C_2H_6$  of sodium resonance radiation, means that transfer of energy from an energy-rich  $C_2H_6$  molecule (in contrast to  $C_2H_4$ ) to a sodium atom is hardly likely to occur. Thus the objection to (1) that



<sup>18</sup> Bawn and Dunning, *Trans. Faraday Soc.*, 1939, **35**, 185.

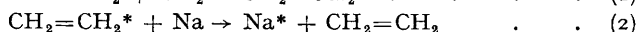
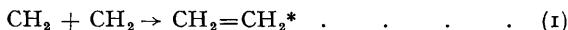
<sup>19</sup> Minkoff, this Discussion.

<sup>20</sup> Norrish and Smith, *Proc. Roy. Soc. A*, 1940, **176**, 295.



does not occur<sup>18</sup> hardly has much force. Energy transfers are highly specific and the clue to their likelihood with sodium may well be found in the converse experiments on quenching of sodium radiation.

**Dr. C. E. H. Bawn** (*Bristol*) said: Dr. Walsh has suggested that the triple-body collision process,  $\text{CH}_2 + \text{CH}_2 + \text{Na} \rightarrow \text{C}_2\text{H}_4 + \text{Na}^*$ , which was ruled out owing to its infrequency, might be replaced by the two-stage process



in which energy-rich ethylene molecule may transfer its energy to a sodium atom. Assuming that (1) is possible, experiment and theory show that reactions of this type do not occur at every collision but have an appreciable steric factor. Under our experimental conditions, in which the total pressure was 0.001 to 0.01 mm., the mean-free-path of the  $\text{CH}_2$  formed is of the order of the diameter of the reaction vessel and collisions leading to association would be extremely infrequent. The association reaction would most probably be a wall reaction, since other evidence indicates a high accommodation coefficient for  $\text{CH}_2$ , and under these conditions the excitation energy would be lost. The same argument applies to the second stage of the reaction and, even if we assume  $\text{CH}_2=\text{CH}_2^*$  of long life, the energy exchange would be a very improbable process, owing to the very high frequency of wall collisions (pressure  $\text{Na} = 10^{-3}$  mm.).

I agree that further information as to the nature of the energy-rich particle leading to *D*-line emission, viz. whether  $\text{Na}^*$  or  $\text{NaBr}^*$ , could be obtained from quenching measurements, and this was the method originally used with Na-halogen flames to prove that the energy-transfer agent was  $\text{NaHal}^*$ .

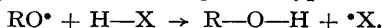
The absence of luminescence in reactions giving a monoradical (R) is of greater significance than is assumed by Dr. Walsh. In no case has luminescence been observed with associations of the type  $\text{R} + \text{R} + \text{Na} \rightarrow \text{R}-\text{R} + \text{Na}^*$ , and a very large number (> 50) of radical types have been studied, including those containing double bonds.

**Dr. E. W. R. Steacie** (*Ottawa*) said: In connection with Part II of the paper of Hinshelwood *et al.* the results are in agreement with earlier investigations which indicated that the frequency factors remain approximately constant down the series, while the activation energy falls off to about  $\text{C}_4$  and then remains virtually constant. If the relatively small inhibition by NO is taken at its face value, then the results for the uninhibited reaction are not much affected by chain processes. However, the falling-off in rate at low pressures for, say, *n*-butane is much too large for so complex a molecule, and would certainly indicate the "freezing" of most of the degrees of freedom. It seems to me, however, that there is considerable doubt if maximum inhibition really corresponds to the complete suppression of chains. In the case of *n*-butane there are three possible modes of decomposition: to  $\text{C}_4\text{H}_8 + \text{H}_2$ ,  $\text{C}_3\text{H}_6 + \text{CH}_4$ , and  $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ . The products indicate that all three occur. However, it is known<sup>21</sup> that the products of the NO-inhibited reaction are identical with those of the uninhibited reaction. If the inhibited reaction is chain-free then the chain process and the non-chain processes must fortuitously lead to the same very complex mixture of products. It seems to me, therefore, most unlikely that the maximally inhibited reactions are simple unimolecular changes.

**Dr. W. A. Waters** (*Oxford*) said: The work of Cullis and Hinshelwood has indicated that the active peroxides involved in the vapour-phase oxidation of hydrocarbons undergo two types of breakdown. They may either give inactive products, or, alternatively, may split to two active products which cause chain-branching. In this connection the outcome

<sup>21</sup> Steacie and Folkins, *Can. J. Res., B*, 1940, **18**, 1.

of the study of the liquid-phase oxidation of tetralin by Dr. A. Robertson and myself is cogent. This first gives tetralin hydroperoxide, and we have shown that although the decomposition of this hydroperoxide in solution is substantially of first order, corresponding to the simple fission,  $R''CH-O-OH \rightarrow R''CH-O^\bullet + \bullet OH$ , only about 50 % of the radicals  $R''CH-O^\bullet$  and  $\bullet OH$  appear to get "free" enough to react with adjacent solvent molecules by reactions of the general type,



The remainder of the decomposition can be accounted for by the chain-breaking process  $R''CH-O^\bullet + \bullet OH \rightarrow R''C=O + H_2O$  between radicals which have not had time to separate.

Prof. Hinshelwood has stressed the point that gas-phase oxidations occur much more easily with normal paraffins than with branched-chain paraffins. Liquid-phase autoxidation gives exactly the opposite order of stability. However, these studies deal with peroxide formation rather than peroxide breakdown, and the facilitation of the complete vapour-phase oxidation may be due to the fact that secondary hydroperoxides, from normal paraffins, are much less stable than tertiary hydroperoxides, which would be formed from branched-chain paraffins.

**Prof. Sir A. C. Egerton** (*London*) said: Prof. Hinshelwood's contribution on "The kinetics of hydrocarbon reactions" is of much interest to me: particularly because of the work done in my department at the Imperial College by Dr. Harris and Dr. Young on the slow oxidation of butane and of propane. The main feature of that work was the analysis of the products of combustion at various stages of the oxidation by both chemical and absorption spectra methods. In all such work, I do not think we shall be on sure ground until the experimental facts are more definite, and our efforts on resuming such work are directed towards improving methods for the analysis of peroxides and aldehydes where they are present together in the products, as indeed they usually are. We find that aldehydes interfere with the determination of peroxides; for instance, for a quantity of aldehyde equal to that of ethyl hydrogen peroxide, only 59 % of the real amount of peroxide is obtained using the KI method (even with catalyst present). The dialkyl peroxides are particularly difficult to determine and the result of analysis is very sensitive to the quantity of iron catalyst needed to liberate iodine from the KI.

With the general scheme of oxidation and the importance of the alkyl peroxide radical ( $R-O-O^\bullet$ ) and the radical  $\begin{array}{c} RC-O-O^\bullet \\ \diagdown \\ O \end{array}$  from aldehydic oxidation, our work is in agreement, except that it seems to indicate a greater influence of the aldehydes (other than formaldehyde). The statement that methane gives rise to no peroxides is also not in agreement with certain experiments we have made, for, under certain circumstances, peroxides are formed during the oxidation of methane.

Anyone who has worked on the combustion of gases cannot otherwise than be impressed by the underlying similarity in their combustion behaviour, and it seems to me the underlying mechanism must be similar. The mechanism for hydrogen, for instance, has a close relation in forming the radical  $HO_2$  with that of the hydrocarbons in forming such radicals as  $RO_2$ .

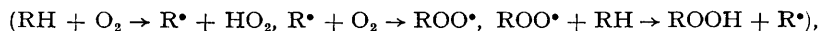
A molecule of a higher hydrocarbon when oxidised has to be stripped or "unravelled" so to speak. After the first few steps which give the peroxide radicals, that unravelling may be very rapid owing to the drastic decomposition of the peroxides (which may not exist as such for any appreciable time) into simple constituents,  $C_2H_5OH$ ,  $CH_3CHO$ ,  $CH_4$ ,  $CO$ ,  $CH_2O$ ,  $H_2O$ , etc.

We are extending the studies of peroxide decomposition which Dr. Harris began: Dr. Emte has succeeded in making *n*-butyl peroxide and we are hoping to study its decomposition.

**Mr. C. F. Cullis (Oxford) (communicated):** Prof. Egerton has pointed out that the results reported in our paper<sup>22</sup> in regard to the influence of higher aldehydes on paraffin oxidation are in direct contrast to those obtained by him and his co-workers. Thus, for example, Pidgeon and Egerton<sup>23</sup> found that addition of valeric aldehyde decreased the induction period of pentane, whereas in our work neither acetaldehyde nor propionic aldehyde exerted any appreciable accelerating effect on the oxidation of this hydrocarbon. It is suggested that these differences may be explained in the following way.

At the comparatively low temperatures employed, aldehyde pyrolysis is normally negligible, but it is very markedly catalysed by the presence of oxygen. The accelerating influence of aldehydes may therefore be attributable to their decomposition reinforcing the normal supply of free radicals. If this is the case, the observed effect would presumably depend largely on the nature of the added aldehyde, this influence being determined by the length of the unbranched carbon chain in the free radical produced. Thus valeric aldehyde might be expected to yield peroxides of high reactivity under conditions where pentane oxidises rapidly, whereas the lower aldehydes would form peroxides which are comparatively stable at the temperatures concerned.

**Dr. G. J. Minkoff (London) (partly communicated):** In the initiation step of hydrocarbon combustion suggested by Prof. Hinshelwood



$HO_2$  and  $R\cdot$  are formed by the action of  $O_2$  on the hydrocarbon molecule.

The fate of the  $HO_2$  will probably be to emerge, partly at least, as  $H_2O_2$ ; the radical  $R\cdot$  will now compete with the molecule  $RH$  for the remaining oxygen, the greater part of the oxygen now combining with the radical  $R\cdot$  to give a peroxide radical and eventually an alkyl peroxide. During the initial stages of the oxidation, we should expect to find that the %  $H_2O_2$  in the total peroxides found decreases as the reaction proceeds, or, for equal times of reaction, as the oxygen content of the mixture is increased. If the initiation is mainly due to hydroxyl radicals, water will be formed, and the peroxides found will contain little or no  $H_2O_2$ . These factors have been investigated by Kooijman,<sup>24</sup> who studied the peroxides formed when different propane-oxygen mixtures were heated to different temperatures for a time of 4 sec. The table above has been computed from his data.

Temp. °C.	$\frac{H_2O_2}{\text{Total peroxides}} \times 100$			
	6% $O_2$ .	10% $O_2$ .	20% $O_2$ .	30% $O_2$ .
380	2	0	3	26
390	15	0	20	37
400	30	4 (?)	30	41
410	43	18	37	33
450	71	61	48	0
480	59	62	46	0

It can be seen from these results that at temperatures above  $410^\circ C$ , the criterion of initial attack by  $O_2$  is fulfilled; below this temperature, a large proportion of oxygen must be present before  $H_2O_2$  is found in the reaction product; it follows that at temperatures below *ca.*  $400^\circ C$ , another mode of initiation, presumably by  $OH$ , is of major importance in the oxidation of propane. These hydroxyl radicals may be formed from the decomposition of a few molecules of alkyl peroxides produced through initial attack by  $O_2$ , this process being so inefficient under these conditions as to become swamped by the "hydroxyl process". No

<sup>22</sup> Cullis and Hinshelwood, this Discussion, p. 116.

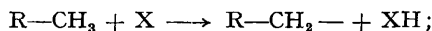
<sup>23</sup> Pidgeon and Egerton, *J. Chem. Soc.*, 1932, 661.

<sup>24</sup> Kooijman, *Dissertation* (Delft, 1942).

evidence is available for the combustion of higher hydrocarbons; it may be inferred, however, that molecules containing a greater number of more vulnerable secondary C—H bonds will be rather more easily attacked by oxygen molecules, so that initiation by  $O_2$  will become more important at lower temperatures as the hydrocarbon chain-length increases.

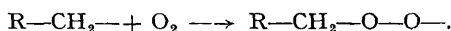
**Prof. A. R. Ubbelohde** (*Belfast*) said: With regard to the papers of Hinshelwood and colleagues, it is not evident that we can dismiss the role of vibrational energy in determining the effect of the size of the molecule on the course of hydrocarbon oxidation, without careful consideration. Vibrational energy does not necessarily affect pyrolysis in the same way as it affects oxidations. It must be remembered that the controlling steps need not be the same in these reactions. Pyrolysis probably involves the breakage of a C—C link. In the case of oxidation of hydrocarbons the attack appears to predominate at the *end* of the molecule and probably involves activation of a C—H link in the first instance. Hydrocarbon oxidation involves a number of steps which might be controlled by the vibrational energy of the hydrocarbon molecules. By way of illustration we can consider three of these.

(1) *Initiation*—i.e. formation of a free hydrocarbon radical by removal of a H atom:



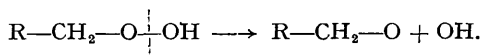
X may be an  $O_2$  molecule but other molecules or radicals may also be effective in certain cases.

(2) "*Quantum-smudging*."



The "molecule" formed in this process will not normally be strictly quantised and will fly apart after a greater or lesser interval unless it is stabilised by collisions in the meantime.

(3) *Chain branching* by breaking O—O link in peroxides, e.g.



With regard to the effect of vibrational energy on these three steps, the general factor to be considered is that, if we start with ethane as the simplest representative of the *n*-paraffins, and increase the chain length by attaching methylene groups, we shall thereby introduce the possibility of coupled vibrations in the molecule with frequencies of lower wave number than the ethane C—C vibration.<sup>25</sup> These vibrations extend throughout the carbon chain, but the coupling of additional methylene groups will not necessarily have much effect on C—H vibrations because of the difference in frequencies between C—C and C—H. Thus increasing the general length of the molecule and thereby lowering the wave number of the lowest vibrational frequency may be expected to influence primarily the reaction steps which involve these frequencies. The first step above, which involves a C—H bond activation, will probably not be very largely affected.

The second step, "quantum-smudging", will be favoured by an increased range of vibrational frequencies. The feature here is the temporary existence of an incompletely quantised molecule formed by binary collisions. Broadly speaking, the more frequencies available in the molecule, the longer the life before it breaks up again.

With regard to the third step, if the vibrational frequency of the O—O bond is sufficiently close to those of the hydrocarbon chain, the coupling of the O—O bond with these vibrations generally will facilitate activation involving the breaking of this bond. But if it differs substantially, the

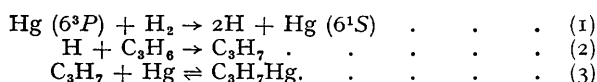
<sup>25</sup> Cf. Ubbelohde, *Proc. Roy. Soc. A*, 1935, **152**, 363, and published data on infra-red and Raman spectra.

O—O bridge will act like a double bond<sup>26</sup> which will not allow the vibrations to pass freely across it. Measurements of the activation energy involved in the pyrolysis of *n*-dialkyl peroxides should give useful information on this point.

**Dr. P. Goldfinger** (*Brussels and Nancy*) said : It seems not to have been sufficiently emphasised that Mr. Partington has found 98 % inhibition of the pyrolysis of ethane and 87 % in the case of propane. These seem to be about the highest figures reported hitherto on NO inhibition. We must admit therefore, that *at least* some part of these reactions follows a chain mechanism. Now in the case of butane Steacie<sup>27</sup> has argued that since the composition of the pyrolysis products, within the limits of error, are the same for the inhibited and uninhibited reaction, it is difficult to conceive two different mechanisms for them. The analysis of the decomposition products of the inhibited and uninhibited reactions in different cases will be therefore of great interest. It is conceivable that a partly inhibited chain reaction would give different products from those of an uninhibited reaction but it would be difficult to understand how the same products could originate from different mechanisms.

On the other hand according to Partington<sup>28</sup> the order of the reaction for *n*-hexane (at 530° c., from 25 to 220 mm.) and for cyclohexane (at 550° c., from 25 to 215 mm.) is 1.0 in the absence, and 1.5 in the presence, of NO. This is exactly what must be expected from Rice-Herzfeld-type mechanisms, as may be seen from general schemes worked out by Goldfinger, Letort and Niclaude,<sup>29</sup> for a chain reaction in which the principal chain rupture is a collision of two radicals with a third body, which is in one case the primary product (first order) and in the other, an added substance as NO (1.5th order).

**Dr. C. H. Bamford** (*Maidenhead*) said : Unpublished experiments by Mrs. Bamford have shown that when mixtures of hydrogen, mercury vapour, and propylene are irradiated by mercury resonance radiation the following reactions occur :



The equilibrium in (3) lies well over to the right at 20° c. The attack of propyl radicals on mercury will be a very serious disturbing factor in Robb and Melville's experiments, since the removal of mercury atoms will reduce the rate of formation of atomic hydrogen. That there is in fact a large decrease in the concentration of free mercury atoms on the admission of small quantities of propylene to an irradiated mixture of hydrogen and mercury is shown by the following figures. The % absorption of 2537 Å. is an indication of the concentration of mercury vapour.

(C <sub>3</sub> H <sub>6</sub> ), mm.	% Absorption.
0	29.8
0.025	19.0
0.25	8.5
1.75	4.6

Incident intensity :  $1.55 \times 10^{14}$  quanta/cm<sup>2</sup>/sec

Initial (Hg) :  $5 \times 10^{-4}$  mm.

(H<sub>2</sub>) : 10 mm.

Thus the addition of 0.25 mm. C<sub>3</sub>H<sub>6</sub> is sufficient to cut down the rate of production of hydrogen atoms by a factor of 3.5. In Robb and Melville's experiments the times taken in a typical run for the MoO<sub>3</sub> to reach a standard blueness were in the ratio 2 : 1 (with and without C<sub>3</sub>H<sub>6</sub>). It

<sup>26</sup> Ubbelohde, *loc. cit.*, p. 368.

<sup>27</sup> *Atomic and Free Radical Reactions* (New York, 1946).

<sup>28</sup> Private communication.

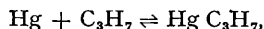
<sup>29</sup> *V. Henri Memorial Vol.* (Liège) (in press).



is clear that the above effect alone is capable of accounting for a good deal of this, and the calculated velocity constants are too high.

The presence of liquid mercury in the reaction vessel was found to have little effect, on account of the slow diffusion of the vapour.

**Prof. H. W. Melville and Mr. J. C. Robb** (*Aberdeen*) (*communicated*): In reply to Dr. Bamford, who suggests that the observed diminution in hydrogen atom concentration in presence of added propylene is due to a reversible reaction,



reducing the rate of generation of atomic hydrogen and that no hydrogenation of the propylene occurs, we wish to make the following observations although his experimental methods and results are at the moment unpublished and unknown to us. We can thus make no comment on his results.

Referring to our paper, it is shown in Tables II and III that estimates of the collision efficiency of the reaction



agree well although measured in two different ways. Table III gives results based on the amount of atomic hydrogen reaching the molybdenum oxide plate (*a*) in absence of propylene and (*b*) in presence of propylene. Table II is based, on the other hand, on the actual number of propylene molecules hydrogenated in the system. This entirely disproves the above criticism and it can be said with certainty that the hydrogen atoms are utilised in a hydrogenation reaction.

However, the point raised by Bamford is not entirely without interest since we have observed that in a system containing a limited amount of mercury, a clean-up of the mercury vapour is eventually accomplished by butyl radicals and it seems to us that this clean-up is probably due to the formation of the mercury dialkyl, although the concentration of the dialkyl would be so low as to make its detection practically impossible. The reaction products have a smell rather characteristic of mercury dialkyls.

We wish to take this opportunity to suggest an explanation of a phenomenon reported by Vanhaeren and Jungers.<sup>30</sup> In their investigations on the hydrogenation of ethylene and propylene photosensitised by mercury vapour, it is reported that at room temperature and in presence of only a saturation pressure of mercury vapour, the reaction of hydrogen atoms with the olefine is much slower than at higher temperatures. Further, if mercury vapour is present in the reaction vessel and also liquid mercury, then the rate at low temperatures and high temperatures is the same. We would suggest the following explanation.

The equilibrium reactions mentioned above occur at low temperatures, the complex formed becoming more unstable at higher temperatures, thus accounting for the slower rate of reaction at low temperatures by the mercury vapour removed. When liquid mercury is present, however, the normal rate conditions are restored since the rate of evaporation of mercury from the droplets is quite sufficient to maintain the normal saturated vapour pressure.

In all our experiments, liquid mercury was present and the pressures employed by us were very much lower than those in the paper quoted, and diffusion effects of mercury would be negligible. Further, it is a feature of our investigations that only a very low quantum input is required to the reaction vessel and the stationary concentrations of atomic hydrogen and free alkyl radicals is so low that the amount of mercury which could be removed by such an equilibrium would be very small.

**Dr. C. H. Bamford** (*Maidenhead*) (*communicated*): Prof. Melville and Mr. Robb have missed the point of my remarks in the first part of their

<sup>30</sup> *Bull. Soc. Chim. Belg.*, 1945, **54**, 236.

statement. I did not suggest that "no hydrogenation of propylene by hydrogen atoms occurs" in their experiments, since the formation of propyl radicals from propylene is a hydrogenation (eqn. (2)). My point was that when propylene is added to an irradiated mixture of hydrogen and mercury vapour the stationary concentration of hydrogen atoms falls for two reasons: (1) the reaction between hydrogen atoms and the olefine, and (2) the attack of the resulting radicals on mercury, which results in a reduction of the quantum input, and the rate of formation of hydrogen atoms. In our experience, (2) is at least as important as (1) under conditions similar to Robb and Melville's. The sum of the two effects is measured in their experiments. The agreement between the results in Tables II and III in Robb and Melville's paper is not significant, and has no bearing on my original criticism. In both cases the quantum input as measured in the absence of olefine was too high.

The results of Vanhaeren and Jungers certainly show that when liquid mercury is present and suitably distributed over the walls of the reaction vessel, sufficient vapour is present (not necessarily uniformly distributed) to absorb most of the incident light. On the other hand, our results indicate that when liquid mercury is present only in the lower portion of the vessel the rate of evaporation is not great enough to maintain saturation pressure. Melville and Robb's results are significant only if their reaction vessel contained a uniform pressure of mercury vapour. Whether or not this was so depends on the distribution of liquids in the vessel. Since there is no mention in the original paper of the presence of liquid mercury it is not profitable to discuss the matter further.

**Dr. C. A. McDowell and Mr. J. H. Thomas** (*Liverpool*) (*communicated*): We should like to mention that our recent investigation of the low-temperature oxidation of gaseous acetaldehyde when peracetic acid is the main product, leads us to postulate an initiation process which is analogous to that put forward by Prof. Hinshelwood and his collaborators, namely,

