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Some Aspects of the Chemistry of Hydrocarbons.

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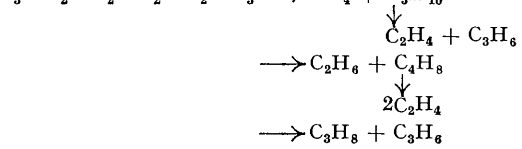
WHILE it may not be wholly unreasonable to fancy that to almost every element there falls some unique and perhaps indispensable rôle in the economy of Nature, it is also evident enough that some occupy the stage more conspicuously than others. The pre-eminence in structural chemistry which carbon owes to its electronic make-up and to its well-balanced position in the electrochemical scale involves almost of necessity the consequence that much of what might be called its functional chemistry is an affair of subtleties and half-tones. This certainly applies to the chemistry of hydrocarbons which at the first approach might have the air of a somewhat uninteresting group of substances but which on closer inspection reveal a rich variety of behaviour.

In the Presidential Address which I delivered last year I referred to the increasing importance of the interplay between the structural aspects and the kinetic aspects of chemistry. I propose now to consider from this point of view a few of the many problems presented by the hydrocarbons.

I shall first say something about what in some ways may be regarded as the most primitive of the reactions of hydrocarbons, namely their pyrolysis. We have known for some time that, under the usual conditions, the thermal decomposition is largely a chain reaction, its speed being reduced to a constant steady fraction of the original value by the addition of quite small amounts of nitric oxide to combine with free radicals. There is room for debate whether the residual reaction which occurs in presence of sufficient nitric oxide is itself a chain reaction of some sort, or whether it is a purely molecular change.

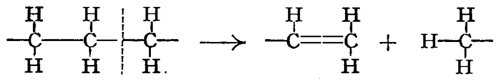
The arguments on the two sides may be briefly summarised as follows. Increasing amounts of nitric oxide reduce the rate of decomposition to a steady limit independent over wide ranges of further additions. This suggests a residual molecular reaction. The alternative is that there is a second kind of chain reaction with carriers unaffected by nitric oxide, or that a steady state is reached where the nitric oxide allows as many radicals to escape as it catches. One of several difficulties about this view is that in conditions where nitric oxide reduces the reaction rate of ethane to less than five per cent. it reduces that of various other paraffins only by about half, and yet the chain-propagating radicals to be assumed in the various cases would be closely similar. The fact that the products of inhibited and uninhibited reactions are nearly the same is not very good evidence either way, since radical mechanisms quite frequently work out to give overall products identical with those of a molecular reaction. One result which would be conveniently explained by the hypothesis of an unrepressed chain reaction is that the residual decomposition rate with excess of nitric oxide is roughly proportional to the power 1·5 of the hydrocarbon pressure. But this law is perhaps hardly established accurately enough or over a wide enough range to constitute unambiguous evidence, and it may simply be an approximate expression of the well-known transition from the first to the second order which unimolecular reactions can show.

I mention this matter as one which we must hope soon to clear up, but the main trend of my remarks will not be seriously affected by the answer. Let us take the example of *n*-hexane which has recently been re-studied by Partington and Danby in this laboratory. The products of the NO-inhibited decomposition are consistent with the occurrence of the series of reactions shown below. (Cf. Burk, Laskowski, and Lankelma, *J. Amer. Chem. Soc.*, 1941, **63**, 3248.)



$$\begin{array}{lll} CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3 & \longrightarrow & CH_4 + C_5H_{10} \\ & & \quad\downarrow \\ & & \quad C_2H_4 + C_3H_6 \\ & \longrightarrow & C_2H_6 + C_4H_8 \\ & & \quad\downarrow \\ & & \quad 2C_2H_4 \\ & \longrightarrow & C_3H_8 + C_3H_6 \end{array}$$

These are all molecular reactions of the type :



$$-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\vdots-\underset{H}{\overset{H}{C}}- \longrightarrow -\overset{H}{C}=\underset{H}{\overset{H}{C}} + H-\underset{H}{\overset{H}{C}}-$$

Auxiliary experiments showed that most of the pentene and a little of the butene would suffer a subsequent decomposition during the experiments, and on this basis the nature and proportion of products can be accounted for.

In the scheme represented above the two interesting matters are (*a*) the relative probabilities of rupture at the first, second, and third C–C links, (*b*) the question as to which end of the broken bond captures the hydrogen atom and which goes to form part of the double bond.

These two questions arise without fundamental change if a chain mechanism is assumed to apply even to the inhibited reaction. For at each fresh cycle of the chain a radical of some kind would have to remove a hydrogen atom from hexane giving one of the three following :

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2—$$
$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\underset{|}{C}H{\cdot}CH_3$$
$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}\underset{|}{C}H{\cdot}CH_2{\cdot}CH_3$$

Each of these would then have to split yielding an olefin and an alkyl radical (which would in turn yield the paraffin product by attacking fresh hexane). The problem of where the chain ruptures, and of the factors determining the capture of the H atom, remains. (In fact it should be remembered generally that many chain mechanisms involve as essential stages the decomposition of a complex radical, and that this process presents problems which are not essentially different from those met in the consideration of molecular reactions.)

On the basis of the scheme given for hexane, what is found is that (*a*) the probabilities of rupture are in the ratio :

C_{1-2}.	C_{2-3}.	C_{3-4}.
3·9	2·5	1

and (*b*) that the shorter carbon residue takes the hydrogen and becomes paraffin, while the longer furnishes the olefin.

The chance of the products

$$CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 + C_2H_6$$

is more than ten times that of

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + CH_2{:}CH_2$$

The case of butane has been investigated by Steacie and Folkins (*Canadian J. Res.*, 1940, **18**, *B*, 1), the relative probability of C_{1-2} and C_{2-3} rupture being nearly equal.* Here the problem of the H-atom capture does not arise.

The interpretation of facts such as the above may involve considerations of two kinds, each of general interest and importance, namely the dynamics of carbon atom chains on the one hand, and the electronic properties of hydrocarbon systems on the other.

First we may ask what may be learnt from the modes of vibration of the carbon skeleton itself. According to the calculations of Pelzer (*Z. Elektrochem.*, **1933**, **39**, 608; cf. also Slater, *Nature*, **1947**, **160**, 576) on a classical system of n equal masses in a linear chain, the chance that a critical amplitude is reached in the relative displacement of two adjacent masses is the same for each position in the chain. The inference from this would be that the chances of C_{1-2}, C_{2-3}, and C_{3-4} ruptures would be equal. For butane this appears to be true of C_{1-2} and C_{2-3}, and for hexane the probabilities are, at least, of the same order of magnitude, though they are by no means precisely equal.

I have worked out the relative amplitudes for the three linear normal modes of *n*-butane and for the five corresponding modes of *n*-hexane, the results being as follows :

n-*Butane.*

	C_{1-2}.	C_{2-3}.	C_{3-4}.
Mode 1	0·50	0·70	0·50
2	0·70	0	0·70
3	0·50	0·70	0·50

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* The probabilities of rupture are calculated from the proportions of products with correction for the fact that there are inherently two chances of C_{1-2} or C_{2-3} breaks to one of a C_{3-4} break with hexane, and two of a C_{1-2} break to each one of a C_{2-3} break with butane, *e.g.*, with butane the ratio $\frac{CH_4}{C_2H_6} = 1{\cdot}92$ and $\frac{C_3H_6}{C_2H_4} = 2{\cdot}04$, but allowing for the fact that C_{1-2} is equivalent to C_{3-4}, these must be divided by 2 to give the relative probabilities of rupture.

n-*Hexane.*

	C_{1-2}.	C_{2-3}.	C_{3-4}.	C_{4-5}.	C_{5-6}.
Mode 1	0·58	1	1·16	1	0·58
2	1	1	0	1	1
3	1·16	0	1·16	0	1·16
4	1	1	0	1	1
5	0·58	1	1·16	1	0·58

It is clear that sometimes the middle breaks will be favoured by the greater amplitudes of the displacements between the appropriate carbon atom pairs, and sometimes not. If all the modes are excited in collisions with equal ease there will be complete averaging, as Pelzer showed on the basis of the general Maxwell–Boltzmann equation. If we wish to explain a certain preference for C_{1-2} breaks with hexane and a relative infrequency of C_{3-4} breaks on a purely dynamical basis, we shall have to invoke more specific influences.

Mr. R. P. Bell has calculated the distribution of zero-point vibration amplitudes for various straight carbon chains and finds that the departure (Δ) of the link fron its equilibrium length is greater for terminal links than for others. The values of Δ^2 for the straight C_6 chain are 0·678, 0·645, and 0·640 respectively for C_{1-2}, C_{2-3}, and C_{3-4}. This factor would tend to operate in the required sense.

Another possibility is this : it might so happen that one or other of the modes which give no relative displacement of the C_3 and C_4 atoms is excited with special ease. I do not at present know of any special reason why this should happen, but I mention the matter specifically because it is one which might be susceptible to investigation by sound-dispersion measurements of the kind which led Alexander and Lambert to detect what may well be alternative modes of activation of acetaldehyde. It is hoped that this study may be extended to hydrocarbons with the object of finding out more about the excitation of the vibrations of the carbon skeleton.

Another line of attack which, however, seems to offer rather formidable difficulties is the further analysis of those parts of the infra-red spectrum which are associated with the skeleton vibrations of the carbon chain.

While we may hope for considerable advances in these directions it remains possible that for the group of facts which I have been discussing an electronic rather than an atomic explanation may be required.

The second question raised, namely which end of the ruptured chain takes the hydrogen atom, certainly seems to require interpretation in terms of electronic ideas. Perhaps, therefore, this may be a suitable opportunity to say something about this subject which is developing in a very interesting way at the present time.

Before discussing theoretical questions, I might remind you of one of two other phenomena which have probably to be discussed in similar terms. One is the tendency of longer alkyl radicals to break down into an olefin and a methyl group—a phenomenon of particular importance in the chain transfer process of polymerisation reactions. This type of process may become of such prominence that a long-chain polymer can, as Melville has shown, give a radical which sheds successive olefin molecules by the exact inverse of the polymerisation reaction by which it was formed.

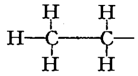
Older qualitative theories have had relevant things to say about the problem. For example, it has been customary in the past to speak of varying degrees of electronegativity of alkyl radicals and to suppose that radicals with relatively greater electron attraction would draw hydrogen from radicals with less. Again, alkyl groups are normally credited with the ability to repel electrons away from themselves to other parts of molecules, ethyl being more effective than methyl in this respect. Then again, various authors, including Werner and Flürscheim, have exploited the idea that in systems of the type A–X–B a strengthening of the bond X–A leads in general to a weakening of the bond X–B.

There are two important sets of general inferences from experimental facts that should also be relevant to the question. First, as judged from effects on the strengths of acids, alkyl groups repel electrons, and multiple carbon bonds attract them. Secondly, as judged from the force constants involved in the C–H vibrations in the infra-red spectrum of hydrocarbons, the tightness of binding of hydrogen to carbon decreases progressively in the structures :

$$\mathrm{CH}\vdots\mathrm{CH};\ \mathrm{CH_2{:}CH_2}\ \text{and}\ \mathrm{CH_4};\ \mathrm{CH_3{\cdot}CH_3};\ \mathrm{CH_3R},\ \mathrm{CH_2},\ \text{and}\ \mathrm{CH}.$$

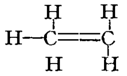
Turning now to inquire what recent theory can offer in the way of general principles, we find an evolution of ideas, due to Mulliken, Wheland, Coulson, Walsh, and others, which aim at accounting for the subtler properties of the C–H and C–C bonds. For convenience I shall classify these ideas under headings, though they are to a considerable extent interrelated.

(1) The first development to which I shall refer is the notion that the bond of a hydrogen may be weakened, with corresponding strengthening of an adjacent C–C bond. In terms of the mathematical theory, which expresses the actual state of things as a superposition of other states which may not actually exist, it is said, for example, that the radical



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\!{-}\overset{H}{\underset{H}{C}}{-}}$$

partakes partly of the nature of



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{=}\overset{H}{\underset{H}{C}}}$$

As Rice and Kossiakoff have pointed out, the possible alternative forms of the radical increase as one passes from a primary through a secondary to a tertiary alkyl radical of the same molecular weight. This by a well-known principle implies a greater stability and, probably, greater ease of formation of the branched radicals, and is not inconsistent with the fact that the binding of secondary and tertiary hydrogen atoms in hydrocarbons is weaker than that of primary carbon atoms. Rice and Kossiakoff see in this one of the principal factors governing the pyrolysis, but I am not clear how far it gives the answer to the two typical questions which I mentioned above in this connexion.

(2) Another important line of thought, closely related to the above, is that of the delocalisation of electrons in the bonds of saturated hydrocarbons. Delocalisation in unsaturated and conjugated systems is a well-defined phenomenon to which reference will be made later. In saturated systems it is a more subtle business, but probably lies at the basis of phenomena of great interest. It has been discussed especially by Coulson (*Quart. Reviews*, 1947, **1**, 144). The essential thing to note for our present purpose is that an electron of a C–H bond is not regarded as completely localised between the particular carbon and the particular hydrogen, and that the extent to which this electron is supposed to participate in other bonds is a function of the symmetry relations of the system. For example, the wave function for the three hydrogen atoms of CH_3, *regarded as a group*, is of the right symmetry to intereact with and to enter into delocalisation phenomena with the wave function associated with the fourth carbon bond. This effect is conveyed to some extent by the symbol $H_3{\equiv}C{-}$, and is referred to as hyperconjugation. Coulson defines the condition necessary for delocalisation and stabilisation as the existence adjacent to a bond, but not actually part of it, of a group able to provide a molecular orbital of the right symmetry to combine with the electrons of the localised bond. It seems likely that the methyl group would play a special rôle in this respect in hydrocarbon chemistry, and indeed methyl groups do appear to exert influences of special kinds.

The binding of the hydrogen atoms in methane, as inferred from force constants, is greater than that in ethane : but the binding in ethane is greater than that of the hydrogen atoms in a CH_2 group of a longer paraffin. Furthermore, it is well known in various connexions that the electron-releasing character of the methyl group is specially great and reaches a very high intensity with the combined action of the three methyl groups of tertiary butyl. A further example of the peculiar influence of methyl groups will emerge presently. It is tempting to connect all these characteristics with the symmetry and the delocalisation phenomenon, though how far this idea will support quantitative testing is at present hard to say.

Returning for a moment to the problem raised above, the greater binding of the hydrogens in ethane as compared with those in CH_2 chains would provide a reason why the fragments formed by the incipient rupture of a C_6 chain should rearrange themselves to give

$$CH_3{\cdot}CH_3 + CH_2{:}CH{\cdot}CH_2{\cdot}CH_3$$

rather than

$$CH_2{:}CH_2 + CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3,$$

a greater combination of group orbitals being possible in the first case than in the second. Similar principles might indeed provide a partial explanation of why higher alkyl radicals should shed the symmetrical CH_3 group leaving an olefin of lower molecular weight (chain transfer in polymerisation reactions), and possibly even of the fact that, when a six-carbon chain breaks, $C_1 + C_5$ fragments are preferred to $C_3 + C_3$, C_1 having a great advantage in ease of delocalisation over C_3 but C_3 relatively little over C_5.

(3) The third respect in which theoretical ideas are developing is in connexion with the actual polarity of C–H bonds. In the C–H bonds of methane, Coulson argues from the nature

of the overall electron distribution that the carbon atom constitutes the positive end and the hydrogen atom the negative end of the dipole. The four electrons of tetrahedral carbon are hybridised from three *p* electrons and one *s* electron and have thus predominantly *p* character. Now it is considered that *s* electrons are more closely held than *p* electrons. Therefore, it is argued by Walsh that as carbon passes to states where its valencies possess more *s* character than in methane, so it should become more electronegative towards hydrogen. In ethylene the hydrogen atoms are held by bonds hybridised from *s* with only two *p* electrons and thus have in fact more *s* character : in acetylene this is still more so, since the H atoms are held by bonds hybridised from *s* and *p*. The result should be a reversal of the C–H dipole, with the carbon assuming the rôle of the negative end.

Here I may refer to the work of Bell and Thompson who have shown that, as far as the treatment of bending vibrations of substituted benzene derivatives is concerned, it is expedient to assume a negative carbon and a positive hydrogen.

I shall pass now to consider the oxidation of paraffin hydrocarbons, a subject in which very remarkable phenomena declare themselves.

It should first be mentioned that two fairly distinct types of reaction have to be distinguished, namely the so-called high-temperature and low-temperature mechanisms. The former governs the course of events with methane, the oxidation of which only occurs with appreciable speed at temperatures above 400°. It seems to depend upon chain reactions involving very primitive molecular fragments, such for example as the O atoms and CH_2 radicals postulated by Norrish for the case of methane itself. The low-temperature mechanism comes more and more into evidence as we pass from methane to butane, and with the higher hydrocarbons it is in operation at temperatures as low as 150°. The high-temperature mechanism provides a study in the resolution of reactions into their simplest steps, while the low-temperature mechanism illustrates some interesting subtleties of hydrocarbon chemistry.

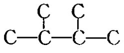
To summarise very briefly indeed the relevant kinetic facts, which have been fully treated elsewhere, we believe the reaction to be initiated by the removal of a hydrogen atom from the hydrocarbon by an oxygen molecule. The radical formed combines with more oxygen to give R–O–O– which attacks more hydrocarbon to give R–O–O–R′. The highly characteristic kinetics are due to the slow branching of reaction chains by the resolution of the peroxide into two radicals of the type R–O–. The rate of oxidation depends upon the initiation rate, ϕ, and upon the branching rate, μ, and the expression for the reaction velocity contains a factor of the form $\phi/(1 - c\mu)$ where c is a constant.

Structure of the hydrocarbon can influence both ϕ and μ, but the reaction rate is much more sensitive to the latter because the condition for rapid oxidation is precisely that $c\mu$ should approach unity. In these circumstances the term $1/(1 - c\mu)$ changes rapidly with change in μ itself. The oxidation rate, therefore, gives a magnified and sensitive measure of the influence of the structure of R on the stability of a peroxide of the type R–O–O–R or R–O–O–R′. It is chiefly on this subject that I am now going to speak.

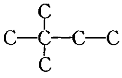
The experimental results obtained during the last year or so by Mr. Cullis and Mr. Mulcahy show that the rate of oxidation increases with extraordinary rapidity with increase in the length of the chain in the normal paraffin series, the values relative to pentane being as follows :

Propane.	Butane.	Pentane.	Hexane.	Octane.	Decane
0·1	0·5	1	7·5	200	1380

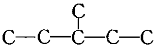
The influence of branching in the chain is equally remarkable, as is shown by the following figures which refer to the relative oxidation rates of isomeric hexanes :


$C-\overset{C}{C}-\overset{C}{C}-C$

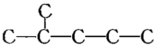
1


$C-\overset{C}{\underset{C}{C}}-C-C$

12


$C-C-\overset{C}{C}-C-C$

60


$C-\overset{C}{C}-C-C-C$

560

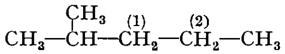
C—C—C—C—C—C

1580

These results contrast in the most striking manner with the relatively small influence of structure on the rate of pyrolysis.

In interpreting these two sets of results we have to bring under one heading two apparently rather diverse factors. Branching of the hydrocarbon chain and lengthening of it have opposite effects. Formally, this is accounted for if we attribute to the methyl group an influence antagonistic to rapid oxidation, and if we further assume that its effect is damped (not enhanced) by intervening CH_2 groups. If, without inquiring further for the moment into its nature, we ascribe such an effect to the methyl group, then the results for the straight and the branched chain paraffins can be correlated.

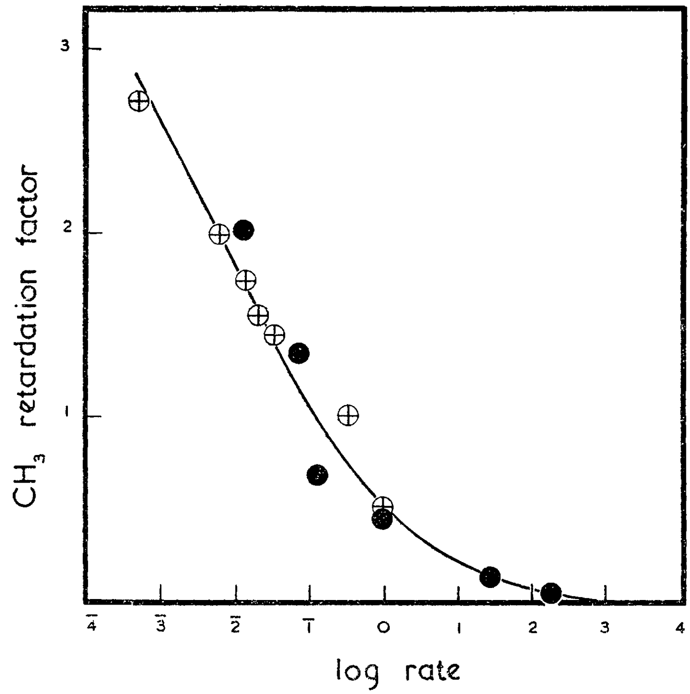
Let us ascribe to the methyl group an antagonistic influence represented by 1·0 unit when it acts at an adjacent carbon atom, 1/3 when at a carbon atom one removed, and 1/9 when at an atom two removed. We further assume that the influences of all the methyl groups are additive. For example in



$$\mathrm{CH_3{-}}\overset{\mathrm{CH_3}}{\mathrm{CH}}\mathrm{{-}}\overset{(1)}{\mathrm{CH_2}}\mathrm{{-}}\overset{(2)}{\mathrm{CH_2}}\mathrm{{-}CH_3}$$

the influence at (1) is $1/3 + 1/3 + 1/3 = 1{\cdot}0$
while that at (2) is $1 + 1/9 + 1/9 = 1{\cdot}22$.

In any given hydrocarbon it is easy to find at which carbon atom this resultant effect is *least* and to suppose that oxidation occurs at a rate which is some function of this factor.



Black circles ; straight-chain paraffins.
Crossed circles ; branched-chain paraffins.

The minimum values for various hydrocarbons are plotted in the Figure against the logarithms of the relative oxidation rates, the points referring to branched and unbranched hydrocarbons being distinctively marked. It is seen that both sets obey one functional relation, which seems to make out a prima facie case for the methyl group as the principal agent.

In the light of what was said above, it would seem that the determining factor is the stability of the peroxide R–O–O–X (where the bond R–O is formed at the point in the R chain least subject to the influence of the methyl). The natural conclusion is that the stability of the peroxide is increased by the electron-repelling tendency of the methyl group, a conclusion which I now prefer to the one provisionally entertained in a previous discussion. This matter needs a little further clarification. It is related to several other facts to which reference must first be made.

In the bimolecular hydrolysis of alkyl halides by hydroxyl ions, increasing chain length diminishes the rate of reaction (see A. G. Evans, " The Reactions of Organic Halides in Solution ", Manchester U.P., 1946). The usual explanation of this is that an *increased* electron-repelling power of the *longer* alkyl groups causes greater resistance to the approach of the negative hydroxyl ion to the seat of reaction. This was the analogy which seemed at first sight to guide the interpretation of the results on chain length and oxidation rate. Such an interpretation, however, fails to deal at the same time with the straight and the branched chains, which can be satisfactorily treated in the way I have just mentioned, namely by assuming that intervening CH_2 groups *diminish* the effect of methyl. When one looks more carefully at the general question of the relative electron-repelling powers of longer and shorter alkyl groups it is seen not to be so clear-cut.

Some of the evidence may be summarised as follows :

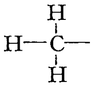
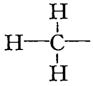
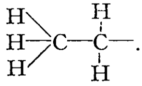
(1) Bond strength between carbon and halogen *decreases* and reaction rate with sodium *increases* with passage up the alkyl halide series. In view of this A. G. Evans attributes the diminishing rate of bimolecular hydrolysis to increasing steric hindrance.

(2) Dissociation constants of fatty acids show varied behaviour, but sometimes lengthening of the carbon chain *increases* the dissociation constant, that is, *diminishes* the electron release which would bind the proton more firmly. Thus, although K drops from acetic acid to propionic from $1{\cdot}86 \times 10^{-5}$ to $1{\cdot}4 \times 10^{-5}$, it rises again to $1{\cdot}48 \times 10^{-5}$ for butyric acid and to $1{\cdot}6 \times 10^{-5}$ for valeric acid.

(3) There is a striking contrast between the small and variable effects referred to under (1) and (2) and the very large effects due to the addition of extra methyl groups, especially of a trio of methyl groups in enhancing the electron release of tertiary butyl compounds.

It would seem in general that a CH_2 interposed between a methyl group and the seat of reaction may both contribute something of its own and damp the effect of the methyl.

The results on oxidation are best covered by the assumptions (*a*) that the peculiar kinetic mechanism brings the electronic effects into special prominence, (*b*) that the stability of the peroxides (in respect of splitting into radicals) is of major importance, (*c*) that the $-O-O-$ bond is *strengthened* by " electron accession ", (*d*) that methyl groups have a special potency in this respect and that their effect is *damped* by interposed CH_2 groups.

The hypothesis that the delocalisation effects in the group  $\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}}$ are of major importance in governing such electron-accession phenomena certainly raises interesting questions, including that of the reason why  $\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}}$ should be more effective than  $\mathrm{H_3C{-}\overset{H}{\underset{H}{C}}{-}}$. In a general way one can see that the symmetry relations in the former are more favourable than in the latter, but quantitative treatment of the problem would be useful.

The kinetic effects which are accounted for by the assumption that the methyl group has in fact this special potency are major ones, and to gather some of the threads together again I will summarise them. First, the remarkable reactivity of tertiary butyl compounds in halide hydrolysis reactions. Secondly, the enormous influence of the methyl substitution in the hydrocarbon oxidations. Thirdly, the vast preponderance, when the hexane chain breaks at the 2–3 position, of ethane and butene over ethylene and butane. Fourthly—though this is a less marked effect susceptible of other interpretations—the somewhat greater tendency for C_{1-2} breaks in the hydrocarbon chains. Fifthly, the great tendency for the shedding off of methyl radicals from longer alkyl radicals.

These matters bring me back to the general theme of hydrocarbon structure and reactivity, and to the fascinating field which it presents for the correlation of experiment, molecular dynamics, and valency theory.

Perhaps I may here mention the fact that some of my colleagues in this laboratory are at present studying the influence of substituents of various kinds, including unsaturated groups, on the oxidation and pyrolysis rates of hydrocarbons. I shall not anticipate their results, but mention simply that they raise in yet another form the immensely important question of the transmission of electronic influences along saturated carbon chains. The theoretical understanding of these transmission effects is of special importance, but also it would seem of special difficulty. They are subtle, but, as I said before, we believe that the study of oxidation rates in the gas phase brings them into special prominence.

I will now turn for a moment to a rather different question. Although many of the remarkable phenomena connected with the oxidation of hydrocarbons depend upon the character of the carbon atom, it is only right to observe that the nature of the reaction partner, oxygen, is of hardly less moment. According to the hypothesis which I have discussed, the breaking of the O–O bond in R–O–O–R′ is one of the key processes. Now the ease and sensitiveness of this rupture is not unrelated to the fact that a single link between two oxygen atoms is very much weaker than half a double link. With sulphur the reverse is true, the single S–S link being more than half as strong as the double. It seemed, therefore, a matter of great interest to know whether the characteristics of the oxidation reactions would reveal themselves in the reactions between sulphur and hydrocarbons, and it was perhaps to be expected that they would not. Dr. Bryce has been examining some of the structural relationships. I shall not here anticipate the report which he will be making in due course about this matter, but I will just say that the effect of carbon chain length and structure so strikingly in evidence in oxidation appears to be absent in the sulphur reaction, and that, for example, hexane and dimethylbutane react about equally well with sulphur, although the ratio of the oxidation rates is of the order of a thousand.

As we have seen, certain quite general propositions about valency stand in a very direct relation to kinetic problems, and one naturally wonders how far we are on the road to a fundamental theoretical treatment of hydrocarbon stability and reactivity.

In some ways the application of valency theory to the chemistry of the saturated group is a little disappointing.

Problems such as that of the transmission of influences from one atom to another of a chain, or of the relation in a system X–A–Y between the respective strengths of the bonds A–X and A–Y, seem not yet to be amenable to any very illuminating treatment. On the other hand, marked success has attended the application of the theory to unsaturated systems, notably to quite complicated conjugated ring systems (see Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39; **192**, 16).

The reason for the distinction is in fact of some general interest. Conjugated systems are in the first place amenable to treatment by a special mathematical method. The σ electrons are allocated to the skeleton structure and assumed to retain their places. The π electrons are assigned to molecular orbitals, each described by a wave function which is taken to be expressible as a sum of atomic orbitals: $\phi = c_1\psi_1 + c_2\psi_2 + \ . \ . \ . \ ,$ there being a separate ψ for each atom of the carbon skeleton. The total wave function of the molecule is the product of the wave functions for each π electron. The total density of π electrons on an atom j is given by Σc_j^2 and the order of the bond between atoms j and k by $\Sigma c_j c_k$, the sum being taken for each atom or pair of joined atoms over all the molecular orbitals. Application of the variation method gives a series of equations determing c_1, c_2 . . . and hence the electron densities and bond orders.

The results of the calculations depend upon two kinds of integral, α and β. It is customary in the treatment of series of molecules to take all α integrals involving carbon atoms only as equal to a standard value occurring in the calculation for benzene, and to use an empirical modification of this value for bonds C–X, where X is a hetero-atom in a ring system. The β integrals are put equal to zero for non-bonded atoms, and to a standard value for bonded atoms.

Now it is obvious that this procedure only introduces one element of specificity into the problem (apart from empirical changes in α for hetero-systems), and neglects the sort of factors which would be of great importance in determining the finer details of behaviour for saturated hydrocarbons. The specific factor governing the result is simply the number of neighbours which each successive carbon atom of the skeleton possesses. The calculation achieves great success in accounting for the properties of conjugated carbon ring systems of various shapes and sizes, and, with a single empirical parameter in a given case, for the characteristics of hetero-systems.

It would appear, therefore, that much of the elaborate chemistry of the great class of conjugated hydrocarbon ring systems is essentially a function of geometry alone, and can be understood in broad outline without solving the problem of subtler influences. It is, I think, not without interest that Nature should work in this way.

The factors which would determine second-order effects in the conjugated systems become the most important differences in the saturated systems, and since they remain small they reveal themselves only to experimentation of a subtler kind. Such experimentation must continue, and, it is to be hoped, the mutual interaction between it and the further developing theory will be to the benefit of both.