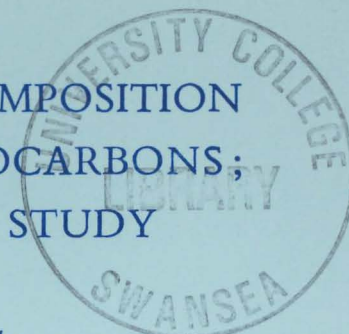


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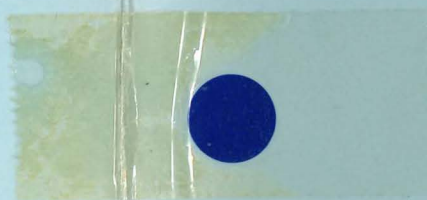
THE THERMAL DECOMPOSITION
OF PARAFFIN HYDROCARBONS;
A CENTURY OF STUDY



*Inaugural Lecture of the
Professor of Physical Chemistry
delivered at the College
on 11th November, 1965*

by

PROFESSOR J. H. PURNELL
B.Sc., M.A., Ph.D.



UNIVERSITY COLLEGE OF SWANSEA

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MY objective tonight is not to give an account of the details of the chemical investigation of the decomposition of the paraffin hydrocarbons but to use the broad picture to illustrate something of the difficulties frustrations and, ultimately, successes of physico-chemical research. It happens also that this particular problem, with which I have been and still am closely concerned, has a history which almost exactly spans the life of my subject as a recognisable discipline. In many respects the pattern of progress in this special research area parallels that in physico-chemical research in general. It is therefore an appropriate topic with which to illustrate also the road to advance in the broader aspects of my subject.

Physical chemistry owes its origins to the work of three men, Arrhenius, Ostwald and van't Hoff. These men, born in the 1850's, recognised independently in their early twenties that the ideas of physics could be applied in chemistry with profit. Arrhenius worked in Ostwald's laboratory for a short while and, over their whole adult life the three men were close friends. In 1887 they founded the first learned journal devoted to physical chemistry, "Zeitschrift für Physikalische Chemie", the first volume of which was written entirely by Ostwald and van't Hoff. All three eventually received the Nobel Prize, van't Hoff being the first Laureate. It was Arrhenius, however, who laid the foundations of reaction kinetics as we now know it and with which subject we are primarily concerned tonight.

The boundaries enclosing physical chemistry have spread far in a century and much of the research conducted nowadays is hardly distinguishable from physics itself. Broadly, the physical chemist seeks to measure, correlate, interpret and then predict chemical effects arising through the transfer of mass and energy. The subject can be divided into three major areas, the structure of matter, equilibria and kinetics. Reaction kinetics, is that part of physical chemistry devoted



to the study of the mechanisms of chemical reaction.

Interest in the paraffins and their properties took on a special significance following the Pennsylvania oil strike of 1859. This venture, which suffered many vicissitudes, inaugurated the new industrial era and I need not elaborate on its impact on our way of life. Prior to and for a while after this, studies of the paraffins were, naturally, in the hands of the organic chemists who were then attempting to rationalise their field and were mostly concerned with identity, structure and classification. As early as 1862, however, we find brief accounts of exploratory studies of paraffin decomposition but real progress dates from 1866 when Berthelot first discussed the mechanism of paraffin breakdown. Subsequently, interest developed and we find in the first issue of the *Journal of the Chemical Society*, in 1873, papers by Thorpe and Young on the effects of temperature and pressure on paraffin hydrocarbons while Schorlemmer discusses the composition of Pennsylvania crude oil. With the years, as the oil industry slowly developed, the need to understand hydrocarbon breakdown became paramount and research effort was greatly intensified world wide.

We thus see that interest in the paraffins was not in the beginning entirely academic and indeed, this pattern has been repeated after each of the World Wars concomitantly with the upsurges in oil production and use. Once more, industrial interest is focussed on reactions of the paraffins. This time because of significant changes in methods of domestic gas production, the prospects of a North Sea gas strike and the rapidly growing petrochemical industry. Thus, my topic of tonight is more than an academic issue and can be seen to relate closely to industrial interests and, ultimately, to our way of life.

The Aliphatic Hydrocarbons

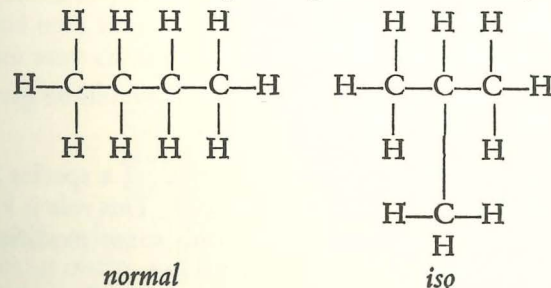
Hydrocarbons, as their name implies are chemical compounds composed entirely of atoms of carbon and hydrogen.

To this extent they represent the simplest kind of organic chemicals, that is, compounds containing carbon. The simplest class of hydrocarbons, known as aliphatic, is that in which the molecules contain simple chains of carbon atoms. The simplest aliphatics are the paraffins. It seems justifiable, therefore, to argue that the thermal decomposition of paraffin hydrocarbons represents the simplest case of thermal breakdown that we may encounter. Extending this view it is logical to suppose that if we are unable properly to describe the mechanism of paraffin breakdown we shall make little progress in our studies of other substances and so a general theory of such reactions will escape us. This, if nothing else, is our justification for placing so much weight on the paraffin problem and in expending so much effort in its investigation.

Paraffin hydrocarbons all have a formula C_nH_{2n+2} where n can be any number. Thus, if $n=1$ we have the substance methane, of formula CH_4 . Higher members of the series with which we are concerned here are:

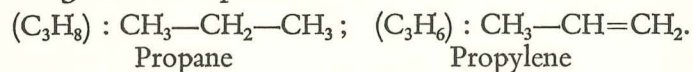
n	Formula	Name
2	C_2H_6	Ethane
3	C_3H_8	Propane
4	C_4H_{10}	Butane
5	C_5H_{12}	Pentane

The element carbon is normally linked to four other atoms in its compounds and, as a result, when n exceeds 3, certain complications arise. For example, butane can have the two structures corresponding to its formula C_4H_{10}



The straight chain form is called *normal* while the branched form illustrated is called *iso*. As *n* increases further, more and more alternative structures become possible. These structures are called *isomers* and are recognisably different molecules each with its own physical and chemical properties.

One other important series of aliphatic hydrocarbons with which we will be concerned is the class known as olefins. These have the general formula C_nH_{2n} , and differ essentially from paraffins in that one pair of carbon atoms in the molecule is joined by two bonds to make up for the hydrogen deficiency. Thus for example, propane and its olefinic analogue can be represented



Like the paraffins, the olefins may have many isomers while, on account of the "double bond", they are chemically more reactive. The olefin usually takes the root of the name of the paraffin, the ending -ane then being converted to -ene; the C_4 olefins, for example, are called butenes. Confusingly, perhaps, the two lowest olefins, C_2H_4 and C_3H_6 are each widely recognised by either of two names, ethene or ethylene and propene or propylene, respectively.

Kinetic Laws

Guldberg and Waage in the 1870's proposed that the rate of a chemical reaction could be expressed in terms of the concentrations of reactants raised to the power in which they appear in the chemical equation. For example, for the reaction



the rate of removal (ρ) of either A or B would be given by

$$\rho = k (A) (B)^2$$

the brackets representing concentration of a species and k some quantity known as *the rate constant*. This rule is known as the Law of Mass Action and with some modification, applies generally.

Shortly afterwards Arrhenius provided the kineticist with one of his most important weapons when he showed empirically that the rate constant varied with temperature according to the equation

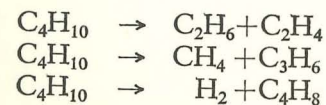
$$k = Ae^{-E/RT}$$

where e is the base of natural logarithms, A is some constant called the frequency factor, E is an "activation" energy, R is the universal gas constant and T represents temperature. From this we see that reaction rates increase remarkably with quite small increases of temperature because of the logarithmic nature of the relationship.

Despite the passage of so many years, the Law of Mass Action and the Arrhenius equation still provide the basis for most interpretive work in reaction kinetics. We now have, of course, some understanding of the theoretical origins of these expressions but this is far from complete. This, however is not the subject under discussion tonight, and I introduce these expressions merely as an aid to later discussion.

Early Studies

Over the period 1865-1930 the decomposition of most lower paraffins had been studied in rudimentary fashion. In most cases the approximate composition of products was known and in some, at least, the rate of breakdown had been measured. At the time, the basic concept of reaction involved only the reactions of molecules and, as an illustration, we may consider the possibilities for *n*-butane. These are



Obviously, when a paraffin decomposes it must always generate an olefin, and further, each molecule generates two new ones so that the pressure in a closed system must rise,

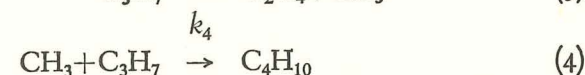
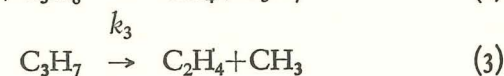
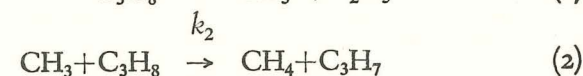
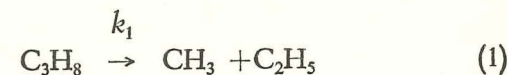
the extent of the rise being exactly equal to the loss of reactant pressure through decomposition. Most workers, therefore, accepting this argument, measured reaction rates by studying rates of pressure rise.

When the Arrhenius equation was applied to these rate data, however, certain grave difficulties of interpretation arose. First, the energy E was, in general, much smaller than thermochemical calculation suggested and, secondly, the factor A , widely identified with the frequency of molecular collision following the work of Lindeman in 1923 and so expected to be about 10^{13} , turned out often to be very much larger. In most cases A was about 10^{18} and in at least one case greater than 10^{20} . How, one asks, can molecules react about a million times faster than they collide? Results such as these clearly undermine confidence in the existing theory. However, no reasonable modification of theory could be visualised at the time and an impasse had been reached. Here the matter might have rested but for the work of F. O. Rice, an emigre Englishman working in the U.S.A.

Early in this century, Gomberg had synthesised some compounds in solution and in the solid state which, surprisingly, were stable although they had an unusual structure in which one of the four bonds of one carbon atom in the molecule was neither attached to another atom nor associated in a double bond. Such a structure apparently defied the laws of chemical combination. Thus, for a paraffin of this sort the formula would be C_nH_{2n+1} and such an entity, having an unpaired electron, and so called a free radical, would be expected to be highly reactive. Gomberg's molecules, however, were very large and could be regarded as a special case, hence, for many years no-one suggested that small radicals such as the paraffinic ones could be made or could ever exist in the gas phase.

In the late 20's, however, the first tentative suggestions that free radicals might be intermediates in reactions had been

offered. Most workers rejected such a proposition since it was felt that as a result the dependence of rate upon concentration of reactants would be of high or complex order. In practice it was found that the value of the exponent in the rate equation was usually small and integral. In 1931, Rice and his co-workers resolved this difficulty by showing theoretically how radicals could participate in gas reactions and yet allow simple kinetics. As an example we may consider a simple scheme which might be considered for the decomposition of propane.



Appropriate algebraic treatment shows that the rate of decomposition of propane is given by the equation

$$\rho = \left[\frac{k_1 k_2 k_3}{2 k_4} \right]^{\frac{1}{2}} (C_3H_8) = k_{exp} (C_3H_8)$$

in other words, the reaction appears to proceed kinetically as the first power of concentration despite its complexity. We see also that k_{exp} is not now describable in terms of a unique A and E and hence A could have any value while $E_{exp} = \frac{1}{2}[(E_1 + E_2 + E_3) - E_4]$ which, since E_1 must be greater than the sum $(E_2 + E_3)$ means that E_{exp} will be less than estimated thermochemically for a molecular split since this gives E_1 .

We see that the scheme outlined, known as a Rice-Herzfeld mechanism, explains at once two major anomalies. More significant still, perhaps, the Rice-Herzfeld schemes

introduced a new concept into reaction kinetics, that of the "chain reaction". Looking at reactions (2) and (3) we see that every time a radical is lost in (2) it is regenerated immediately in (3). Thus, while propane has decomposed there has been no loss of the entity causing decomposition. Hence, unless a reaction such as (4), which removes two radicals, intervenes, reaction (1) need only occur once to bring about total decomposition. The length of the chain is determined solely by the relative rates of (2) and (4) and we now know that chain lengths may vary from one or two to many millions. Rice-Herzfeld type mechanisms may be written for most reactions and can be extended indefinitely to account for experimental results.

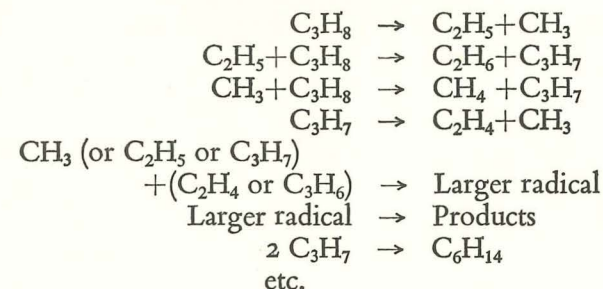
The impact of Rice's chain reaction concept was immediate and unquestionably represents a notable landmark in the physical sciences. However, while it offered a totally new view of the way in which reactions may proceed, it exposed an unhappy experimental situation which, in the event, took twenty five years to remedy.

In the era of exclusively molecular reaction schemes little importance had been attached to carrying out worthwhile quantitative analysis of the product. The reasoning underlying this attitude was simple; if a molecule decomposes molecularly, the products must be predictable. For example, in the decomposition of propane by molecular means we can only visualise the reactions



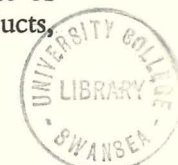
and the only matter of interest, requiring analysis of products, is the ratio $\text{C}_2\text{H}_4/\text{C}_3\text{H}_6$. For this, following the same logic, a single analysis at any time in the progress of a single experiment would suffice. In a chain reaction scheme, however, the system contains not only relatively stable reactant and product molecules but at least two reactive free radicals. Recognition of this demands the postulate of a much more

complicated pattern of events, as for example in this extended but still abbreviated scheme:



From this we see that many products may arise and it is clearly axiomatic then that thorough investigation of chain reactions demands very detailed analyses. It can also be seen that as reaction progresses, the complicating reactions involving C_2H_4 or C_3H_6 in the above scheme become much more probable because these compounds are present in ever increasing amount as reaction proceeds. Thus, analysis must be conducted in the first moments of reaction if information about the elementary processes occurring is to be obtained.

Gas kinetic studies of the type under discussion may in general, be conducted by one or other of two basic experimental techniques. The first, the static method, involves introducing a known amount of reactant into a reaction vessel, observing by some means any physical changes occurring in the system as reaction proceeds, and then removing the mixture in the vessel at some desired time, possibly for analysis. The amount of product material available for analysis is obviously limited by the size of the vessel used and the extent of reaction and with the tedious and unreliable analytical methods of the 1930's, analysis, even quite late in the reaction, was effectively precluded. Thus, workers who chose to employ this approach continued to rely upon the physical measurement, usually that of pressure in the vessel. They thus learned something of the rate of decomposition but nothing about the nature of the products,

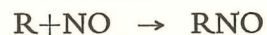


or of the rates of their appearance. Indeed, unless the detailed relationship of products and reactant is known, this approach may yield no useful information at all.

In the second method, the flow technique, the reactant gas is continuously passed through a reaction tube, the effluent being collected by some means, usually refrigeration. This approach yields as much material for analysis as may be required since a given reaction may be prolonged indefinitely. However, the physical complexities of flowing systems which, in addition, are reacting, are such that worthwhile information about reaction rates is only obtained from experimental data by tedious and often unreliable calculation. This was, and by some still is, regarded as more significant than the absence of analytical data and so, early workers most commonly used static systems. In consequence, attempts to interpret data in terms of the new chain concept are seen in retrospect as more ingenious than convincing.

The Inhibition Era.

A quite different attitude to the consequences of Rice's ideas was taken by some. Arguing that since free radicals are highly reactive they should be readily eliminated thus leaving reaction to proceed by what, in principle, should be the simpler molecular modes of decomposition. In 1934, it was found that the gas, nitric oxide (NO), which is unusual in having the odd number of electrons characterising simple radicals and yet exists as a stable gaseous molecule, reduced dramatically the rate of many gas reactions when added in small amount. This, it was presumed, arose because NO in the presence of a radical showed its own radical character and underwent reactions such as

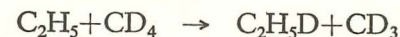


RNO being supposed to be a stable and relatively unreactive molecule. Further study revealed other inhibitors such as propylene and the several butenes.

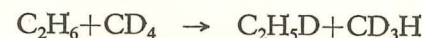
Inhibitors do not totally suppress reaction but reduce the rate only to some lower value; beyond some fixed amount

of inhibitor, no further reduction in decomposition rate occurs. Hinshelwood and his associates, at Oxford, decided that this residual reaction, since it was unaffected by addition of more inhibitor, was a true molecular process and, therefore, that in the absence of inhibitor, paraffin decomposition occurred via concurrent radical and molecular paths. This view was later reinforced by the finding that in the decomposition of n-pentane at 525 Degrees C., the limiting inhibited rate was the same whether NO or propylene was used to inhibit. Since propylene is not a radical its inhibiting action cannot arise in the same way as that of NO and this adds considerable weight to the argument.

Not everyone, however, took this point of view. Steacie in Canada and Pease in the United States led others in arguing that the evidence was equivocal and that total inhibition could correspond merely to a modified chain reaction. In support of their views they brought to bear on the subject in the 1940's the powerful, developing techniques of mass spectrometry and of radiochemistry. They showed for example, that to the best of their analytical ability the products of the uninhibited and totally inhibited reactions were, not only the same, but in the same proportions. Again, experiments at total inhibition in which traces of CD₄ that is, methane containing not hydrogen but its isotope, deuterium was transferred to other hydrocarbons in the system. While the following kind of radical reaction



leading to deuterium transfer can be readily envisaged, the equivalent molecular process



seemed very unlikely both on the grounds of experience and of intuition. This was taken, therefore, as strong evidence that radicals were present at total inhibition. In response, Hinshelwood was able to show that these experiments were in several respects deficient and that with small extension of hypothesis the more reliable data could be

happily accommodated within the molecular theory.

At about this time, 1954, Voevodsky in Russia introduced even more complication into the argument. While agreeing with Steacie and Pease that there was in fact no molecular mode of decomposition of the paraffins, he interpreted his experiments with propane as showing that the inhibition process did not occur in the gas at all, but on the surface of the reaction vessel. The reactive nature of reaction vessels, even of quartz or glass, has been recognised for many years and indeed, most of the work discussed here so far was carried out in vessels deliberately coated with carbon. This device, still quite widely employed, frequently eliminates erratic behaviour and so has been widely supposed to eliminate surface reactions. This, of course, is only the most convenient of several possible explanations. Voevodsky's work, far from settling the issue, confused it, since it raised again the neglected question of surface effects and to confuse the issue further, Voevodsky himself had supposedly eliminated surface effect by coating his reaction vessels with magnesium perchlorate. This substance is now known to decompose to liberate the very reactive oxygen and chlorine in the conditions of paraffin decomposition. The remarkable accelerative effect of minute traces of oxygen on many gas phase reactions, including paraffin decompositions, had been clearly shown by Letort, Niclause and their collaborators in France. Thus Voevodsky's own experiments and consequent interpretation were suspect.

This then is where the problem stood in 1958. After nearly a century of study and twenty five years of most intensive investigation there was no real agreement on the occurrence or otherwise of molecular reactions, on the role of surface reactions, on many quantitative kinetic details and in some cases, even on the identity and distribution of products.

It is pertinent to inquire into the reasons for this situation and, in essence, the explanation is simple. The appropriate technical approach was difficult, relatively unreliable and

lengthy and, in the interests of expediency less suitable methods were employed. The inadequate, and often misleading information these yielded was then stretched beyond the breaking point. No great advance in analytical technique occurred in the twenty five years referred to and, indeed, despite general recognition of the need, little effort was expended in this direction because of an intrinsic academic lack of interest in technique as such. Clearly a breakthrough was needed, and fortunately, it had come in 1953 when James and Martin at the Medical Research Council Laboratories had invented the first viable approach to the chromatographic separation of gases.

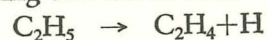
Chromatography is an analytical technique in which some solid or liquid is held static in a bed, often a glass or metal tube, or where possible, as when liquid systems are used, a strip of paper, while a different liquid or a gas is percolated through. In gas chromatography, some inert gas such as nitrogen flows continuously and, when desired, a small sample of the gas for analysis is injected. The various sample components have different affinities for the static material and so flow through the static material at different rates. They thus emerge from the bed or column at different times and their amount can be measured.

By 1958, not only had this technique been put on a technically firm foundation but had been brought to the point where analyses previously requiring days, if they could be done at all, could be carried out in minutes and this with no more than a millionth of a gram of material. From this basis, we, and more recently others, developed experimental techniques for gas kinetic study.

For our earliest studies we chose the decomposition of *n*-butane and it took little time to establish that both minute traces of oxygen and the reaction vessel surface had pronounced effects on the results. Elimination of these undesirable features took much time and effort but was ultimately achieved. The investigation then revealed complicated relationships between products, product distribution

and experimental conditions and these showed conclusively that the decomposition was entirely free radical in nature. Remarkably, with one small modification the broad aspects of the reaction mechanism were described accurately by the scheme developed for n-butane from the basic Rice-Herzfeld proposals of thirty years before.

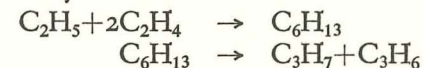
The mechanistic modification introduced was a consequence of the finding that the reaction



which plays an important part, not only in this but other decompositions, was not a simple first order process but, in fact, proceeded at a rate proportional to the 1.5 power of the concentration of C_2H_5 radicals. This turns out to be an interesting finding for theoretical reasons but also explains certain anomalies observed in other systems where C_2H_5 predominates. A further special property of this radical was also recognised in this study. C_2H_5 is the most unreactive entity of its class and so, if produced in significant amount in any reaction will occur in higher concentration than other radicals. It will dominate the radical-radical interactions which terminate chains and hence, although unreactive, will determine the overall kinetic characteristics of reaction since these are largely fixed by the termination step. This finding is of great generality and offers an explanation of many aspects of hydrocarbon decomposition.

Our work on n-butane has since been repeated elsewhere on several occasions and our findings and interpretations confirmed. Thus, a major controversy extending over a quarter of a century and affecting the whole field has been settled. However, the results illustrated only too clearly that previous work could only be accepted with caution and that a total re-investigation of all paraffins was needed. Realising this view, we have since studied the decompositions of ethane, propane and of iso-butane and others too are pursuing the same aim. The general characteristics of the n-butane reaction are observed with each paraffin although in each decomposition, special features are noted.

One very significant finding, which emerged from the ethane study was that even when only 1-2% had decomposed, secondary processes were significant. Quinn showed that secondary reactions such as



were important. The first step above is a polymerisation and the recognition of the importance of the polymerisation decomposition sequence illustrated above has given a new view of reaction mechanism. Following the above idea it is found possible, for most reactions, to write a notional decomposition entirely in terms of a polymerisation-decomposition sequence. This view, as it happens, usually cannot be readily directly verified by conventional experiments because of the extreme complexity of the chemistry involved and the fact that the products are identical with those of simple decomposition schemes. In support of the experimental approach, therefore, we have now undertaken the simulation of reactions on a computer. By this means we can more quickly learn the characteristics of the postulated complex reactions and, then hopefully, use this information to design simple and economical experiments to test the theory.

In the short time available I have been able only to outline the major events in the history of paraffin pyrolysis. In consequence, the issues have appeared much more clearly defined than at any time was the case. Paraffin pyrolysis, of course, represents only a tiny part of the great field of physical chemistry but I hope that this review of its history has shown that research in physical chemistry is rarely straightforward, usually difficult but always interesting. Theoretical ideas come and go, the advent of new techniques sometimes leads to complete re-evaluation of existing concepts. With each change, however, we see inevitably that the systems we study are in fact more complex than we had hoped. While there is undoubtedly elegance in simplicity, the generalising simplification, in reaction kinetics at least,

escapes us. Our recompense for our efforts can only be the recognition that we enjoy what we do and that this advances our knowledge along the path to final understanding of some grand unifying idea.

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