

Phosphorescence, Fluorescence, and Chemical Reaction.<sup>1</sup>

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ONE of the most important theories brought forward during recent years is that known as the radiation hypothesis, which was developed independently by Perrin and by W. C. McC. Lewis. Briefly stated in an elementary way, this theory postulated that molecules in general have no chemical reactivity, and that they become reactive after they have absorbed energy. In order that a specific reactivity be induced, a definite quantity of energy must be supplied to bring each molecule from its initial stage to its reactive state, this quantity being called the critical increment of energy characteristic of the specific reaction.

The Einstein law merely states that in a photochemical reaction a molecule absorbs one quantum of radiant energy,  $h\nu_0$ , and then becomes activated, no assumption being made as to the difference in energy content of the initial and reactive states. The radiation hypothesis states that the difference in energy content of the initial and reactive states, or the critical increment of activation, is a single quantum which can be absorbed from infra-red radiation. The critical increment of energy characteristic of a reaction is neither expressed nor implied in the Einstein law.

It is a simple matter to calculate the critical increment of a reaction from the observed change of the velocity constant with temperature, and to obtain the critical frequency  $\nu$ . Not only must this frequency be one characteristic of the reactant molecules, that is to say, one that can be observed by absorption spectra measurements, but the radiation hypothesis also demands that exposure of the inactive molecules to radiant energy of that frequency should cause the reaction to take place. As a matter of experimental fact, molecules in their inactive states do not show any evidence of being characterised by frequencies equal to those calculated from the critical increments. This in itself is sufficiently significant to arrest attention, but when it was proved first by Lindemann and then in most elegant fashion by G. N. Lewis that molecules do not react when exposed to radiant energy, not only of the calculated frequency but also of a very large range of infra-red frequencies, it was felt on all sides that the radiation hypothesis had been effectively and completely disproved.

The situation thus reached is one of considerable interest. There exist on one hand large and increasing numbers of photochemical reactions which are obviously stimulated by the absorption of radiant energy. If the Planck theory stand fast, the reactant molecules must be activated by the absorption of the energy quanta  $h\nu_0$ , since it is well known that the frequency  $\nu_0$  is characteristic of them. On the other hand, the radiation hypothesis is based on premises which appear to be theoretically sound; nevertheless, it has been proved to be untenable. As a result the general consensus of

opinion has swung over to activation by collision in thermal reactions. It must, however, be confessed that the present position is very far from being a satisfactory one. In the case of true photochemical reactions, it is not possible to believe that activation of the reactant molecules is not produced by the direct absorption of radiant energy. In the case of thermal reactions, the evidence disproves the activation by the direct absorption of radiant energy, and activation by collision has been substituted.

When the obsequies of the radiation hypothesis had been sung, it was felt that the corpse had received decent burial. I venture to point out that this hypothesis may be divided into two parts. The first part is concerned with the critical increment of energy of a reaction, that is to say, the minimum quantity of energy, or rather the exact quantity of energy, which is required to bring a molecule from its initial state to its reactive state. Unless the whole conception of different molecular states be dropped, this conception of a critical increment stands on a sure and firm basis. The second part of the hypothesis, namely, that the critical increment can be absorbed as a single quantum of energy by a reactant molecule, is a pure assumption and one that would only be justified by a knowledge that the properties of molecules are in this respect identical with those of elementary atoms. The uncertainty which attaches itself to this assumption impresses me so strongly that I propose to exhume the body in order that the cause of death may be more fully investigated.

So far as the phenomena of chemical reaction can help us, our knowledge of the physical properties of molecules, and in particular their change from one to other states of energy content, is singularly meagre, and it would seem that little more can be gained in this direction even by the most intensive study of purely chemical processes. I venture to stress this point of view because I believe that the necessary evidence can only be gained from sources of information which are independent of the processes we wish to explain. Such independent sources of information may be found in the phenomena of phosphorescence, fluorescence, and absorption spectra of compounds.

The term phosphorescence is a broad one and includes both photoluminescence and cathodoluminescence, together with certain subsidiary phenomena. The only one of these that can serve our present purpose is photoluminescence, since a knowledge is essential of the frequency of the activating radiation as well as that of the emitted radiation.

Lenard and Klatt established the very important fact that phosphorescent emission is not a truly reversible process. It is only possible to activate a phosphore by means of radiant energy of the same frequency as that of its characteristic absorption band, which lies on the short wave-length side of the

<sup>1</sup> From the presidential address to Section B (Chemistry) of the British Association, delivered at Glasgow on Sept. 6.

characteristic emission band. These investigators proved the complete validity of Stokes's law, and as the result of later work on true phosphorescence, this law has been proved invariably to hold.

The importance of this may at once be recognised if the facts be stated in more scientific phraseology. When an activated phosphore is emitting its characteristic luminescence, each activated molecule radiates a single quantum of energy in passing from the higher energy state to the lower energy state, the total luminescence being the sum of all these radiated quanta. In the process of activation the change from the lower to the higher state is caused by the absorption of that same quantity of energy by each molecule, and in view of the radiation as a single quantum it is legitimate to assume that it is absorbed as a single quantum, nothing being expressed or implied as to the mechanism of the absorption. Each molecule, therefore, requires for its activation a critical quantum of energy  $h\nu_1$ , and the value of  $\nu_1$  may be directly obtained from the measurement of the luminescence. The proof given by Lenard and Klatt and by others that Stokes's law is valid indicates that it is impossible to activate a phosphore by means of radiant energy of the frequency  $\nu_1$ , and that the critical quantum of activation cannot be supplied to a molecule by a singular absorption process. There exists, therefore, in this respect a sharp differentiation between the physical properties of molecules and atoms.

The lethal dose of criticism which killed the radiation hypothesis was based on the experimental proof that molecules are not able to do this very same thing, namely, absorb their critical quanta of activation  $h\nu_1$  at the calculated frequency  $\nu_1$ . The radiation hypothesis was killed because the assumption of the second part was made in ignorance of what molecules can do and cannot do.

It may be argued that the activated molecular states which are responsible for phosphorescence must be essentially different from those which function in chemical reaction, because their life periods are enormous compared with those of chemical processes. The fact remains, however, that in a series of different energy levels the uplift from a lower to a higher level cannot be achieved by the absorption of radiant energy of the frequency corresponding to the energy difference.

It may be pointed out that there is a close similarity between the effective methods of activation in the fields of photoluminescence and photochemistry. In each the activation is achieved by exposing the inactive molecules to radiant energy of a frequency equal to that of a characteristic absorption band of the inactive state, and this frequency is invariably greater than that calculated from the quantum of activation. Stokes's law, therefore, may be said to apply to photochemistry as well as to photoluminescence.

In view of the mechanism of activation which is common to photoluminescence and photochemistry, it is legitimate to inquire into the destination of the excess of the energy absorbed over the critical quantum of activation. The energy quantum absorbed by a single molecule may be denoted by

$h\nu_0$ , and the critical quantum of activation by  $h\nu_1$ , where  $\nu_0$  is greater than  $\nu_1$ , and the question is what happens to the energy difference expressed by  $h\nu_0 - h\nu_1$ .

It is legitimate to assume that the energy difference is radiated as a single quantum  $h\nu_2$ . It may be suggested that this radiation during activation by light of frequency greater than that corresponding to the critical quantum of activation is the origin of fluorescence. Apart from any other argument, it is necessary that the radiation of some energy must accompany the activation of a molecule by light if Stokes's law is generally valid, and the view now brought forward is that under certain conditions this energy can be radiated as a single quantum of fluorescence. Fluorescence, therefore, should always be exhibited during the photo-activation of a phosphore.

The one essential criterion for fluorescence is the existence with a finite stability of an energy level intermediate between the initial level and the super-activated level to which the molecule is raised by absorbing the quantum  $h\nu_0$ . It is by no means necessary that the stability of the intermediate level be sufficiently great for delayed or phosphorescent emission to be visible when the molecule changes from this level to its normal level. The conditions for phosphorescence are far more restricted and rigid, one of these being that the phosphore must be in the solid state. It is therefore not surprising that fluorescence is of far more frequent occurrence than phosphorescence.

The principle of fluorescence radiation must also apply to photochemical reactions, in all of which the activating quantum is greater than the actual energy of activation. Here again the relation should hold that

$$h\nu_0 = h\nu_1 + h\nu_2,$$

where  $h\nu_0$  is the quantum of energy absorbed at the characteristic molecular frequency in the ultra-violet,  $h\nu_1$  is the critical increment and  $\nu_2$  is the frequency of the fluorescence. It would seem, therefore, that the suggested explanation of fluorescence may be put to a very severe test by the quantitative study of photochemical reactions. Some preliminary observations have been carried out at Liverpool by Mr. Leathwood and these give definite support.

It may be concluded that a definite position has been reached which is of some interest. The radiation hypothesis states that the first stage of a chemical reaction is the activation of each molecule of the reactant by the absorption of one quantum of energy, which has been called the critical quantum of activation. Evidence gained from the experimental investigation of the phenomena of photoluminescence gives strong support to the reality of this critical quantum of activation, but entirely disposes of the possibility of a molecule gaining this quantum by a single absorption process. The photochemical activation of molecules has been discussed in the light of the evidence gained from the fields of photoluminescence and absorption spectra, and the destination of the whole of the energy gained by a molecule when it absorbs its

photochemical quantum has been traced. Lastly, the connexion between the observed heat of a reaction and the critical increments of activation, derived by the radiation hypothesis, has been extended to the photochemical quanta, which is an advantage, since the photochemical frequencies can be directly observed by spectroscopic methods. It may even be considered that the exhumation of the radiation hypothesis has been partly justified.

There is no doubt, however, that this partial justification raises the question of thermal reactions in a form which is even more acute than was the case at the inception of the radiation hypothesis. The inability of a molecule to gain its critical quantum of activation by means of a single absorption process has been demonstrated in a far wider field than was covered by the experiments of Lindemann and G. N. Lewis, which as a matter of fact were devised *ad hoc*. Unless some mechanism exists whereby a molecule can gain its critical quantum of activation from a source of infra-red radiation, photochemical activation must be viewed as an abnormal event and the exhumed radiation hypothesis must be re-interred at once and for all time.

I have been led to re-open this question by some recent observations which appear to throw new light on the problem. These observations encourage me to suggest a possible mechanism of activation by infra-red radiation. Some justification may be found in the fact that it offers an explanation of many of the difficulties that have been met with in interpreting the phenomena observed in absorption spectra.

Mr. Hood at Liverpool has succeeded in determining the temperature coefficient of the reaction whereby carbohydrates are photosynthesised from carbonic acid in the presence of pure nickel carbonate; the relation between the temperature and the yield is linear between 5° and 31°. This result is of some interest in view of the fact that pure photochemical reactions have a temperature coefficient of unity. It has previously been shown that: (a) Carbonic acid in aqueous solution is not acted on by white light; (b) carbonic acid when adsorbed on a coloured surface does not react in the dark; (c) carbonic acid when adsorbed on a coloured surface and irradiated by white light reacts to give carbohydrates.

It follows as a necessary conclusion from the facts that the complete activation of the carbonic acid must take place in two stages, namely, partial activation by adsorption with the formation of a molecular state capable of absorbing some rays within the visible spectrum, whereby the activation is completed by photochemical means. Furthermore, the number of partially activated molecules which are able to enter into the final reaction is in linear proportion to the temperature. It is this first stage of partial activation which is of interest in our quest, since it is evident that the adsorption process alone is not sufficient to bring the molecules into a state which enables them to react photochemically under the influence of visible light, the supply of heat energy being necessary to add the finishing touch to the partial activation.

There is a striking analogy here with anisole and the other phenolic ethers and their nitro-derivatives in solution in concentrated sulphuric acid. There can be no doubt that the ether molecules in the acid solution have gained their critical quanta of activation, and yet their activated states must be stabilised in some way, since no measurable sulphonation takes place at ordinary temperatures. When the solution is warmed at 50° the expected reaction proceeds.

Now it is very probable that there is one factor which is common to the two sets of observations, namely, the existence of a complex, that is to say, an adsorption complex of carbonic acid and nickel carbonate in the one and an addition complex or solvate of the ether and sulphuric acid in the other. If the mechanism of complex formation be considered, it would appear that two methods are possible whereby a complex can be stabilised. The most usual case is when two components form a complex with a loss of energy, and such a complex will only be resolved into its components by the supply of energy equal to that lost in its formation. As an example of this type of complex the salt of an organic base such as aniline may be instanced, this type having a positive heat of formation.

On the other hand, it may be suggested that another possibility exists, namely, the formation of an addition complex of two components, one of which yields a definite amount of energy to the other. Such an energy transference, so far as external evidence is concerned, will be an isothermal process. It may further be suggested that the amount of energy given up by the first component to the second component is equal to the critical quantum of activation of the second component. Such complexes will not be formed between any two molecules, but only between two which satisfy the conditions, the criterion being that a molecule of one compound, possibly by loss of rotational energy, can give to the molecule of another compound energy equal to the critical quantum of activation of that molecule. A complex of this type may be denoted by the symbol  $A^{-}B^{+}$ , where  $B$  has gained its critical quantum of activation at the expense of the rotational energy of  $A$ .

Let it be accepted that such complex formation is possible in order that the properties of these entities and their probable influence on the phenomena under discussion may be critically examined. It may first be concluded that, even though the molecule  $B$  has become activated, the reaction characteristic of the activated state will not take place until the energy defect of the molecule  $A$  has been restored. In other words, the activated state of the molecule  $B$  has become stabilised. In the second place, the resolution of the complex into a normal molecule of  $A$  and an activated molecule of  $B$  will be secured by making good the defect in the rotational energy of the molecule  $A$ . The formation of a free molecule of  $B$  in the activated state is no longer a process of direct activation by radiant energy, which has proved to be impossible, but an increase in the rotational energy which, as is known, can be effected by means of infra-red radiation.

It must be emphasised that the temperature is a most important factor, and there must be for every complex a characteristic temperature limit, below which it is completely stable. When the temperature is progressively raised above the characteristic limit, an increasing number of complexes will be resolved in unit time, and the reaction velocity will increase. It may be said, therefore, that the stability of the complexes progressively decreases as the temperature is raised above the temperature limit, and it follows that there must be an upper temperature limit above which the complex will have no measurable stability, and at this temperature the reaction velocity of a simple chemical reaction will reach a maximum and will indeed be instantaneous, if such a word can be applied to a process involving the mixing together of the reactants. The photosynthesis reaction is differentiated by the fact that it consists of two stages, and the temperature limits concern only the stability of the adsorption complex characteristic of the first stage.

The hypothesis of complex formation also offers an explanation of the phenomena of photoluminescence. There is one outstanding fact in connexion with the activation of the phosphorogen in a phosphore which indicates the presence of a complex of the type we are dealing with. In all cases where the activating wave-lengths have been measured, these are longer than those which are characteristic of the phosphorogen in the free state. This at once leads to the view that each phosphorogen molecule has formed a complex with a molecule of the diluent, and within that complex the phosphorogen exists at a level of higher energy content than the normal. The stability of the complex will be determined by the temperature as it can only be resolved into its components by the supply of infra-red radiation to make good the defect in the rotational energy of the diluent molecule. Even though the phosphorogen component is raised to a still higher level by absorption of its characteristic quantum at the ultra-violet frequency, the complex will remain in its stable state provided that the temperature is below the lower limit characteristic of the complex.

An instance of an exactly analogous phenomenon is the very striking fluorescence of benzaldehyde in concentrated sulphuric acid solution. In this case the aldehyde within the complex absorbs and radiates energy without its stability being affected. It may therefore be suggested that even after the phosphorogen has been raised to a higher level of activation than that which it reaches in the actual formation of the complex, the new state is no less stable than the complex itself. If that be so, the whole of the phenomena of photoluminescence which have been previously described will find a simple explanation. There will be a lower temperature limit below which the activated complex will be completely stable, that is to say, no phosphorescence will be observed. When the temperature is raised above the lower limit the region of partial stability will be entered and phosphorescent emission will begin, and progressive rise of temperature will

progressively increase the number of complexes that are resolved and the intensity of the phosphorescence will increase. Since there are present a finite number of complexes, the total persistence of the emission will decrease. At any constant temperature between the lower and upper limits the intensity will have a definite rate of decay. Just below the upper temperature limit where the stability is vanishingly small the persistence will be vanishingly small and the intensity will be the maximum. Up to this stage the phenomena will be identical with those of a chemical reaction, the criterion of intensity of phosphorescence being substituted for the criterion of reaction velocity. When the upper temperature limit is passed the complex will no longer have any stability and will no longer exist. No phosphorescence or fluorescence will be possible, since these depend on the stable existence of the complex with its power of retaining the energy which it absorbs at its characteristic frequency in the ultra-violet. These phenomena are identical with those observed by Lenard and Klatt.

One further piece of evidence, which has hitherto not been mentioned, may now be brought forward. The hypothesis of complex formation demands that the defect in the rotational energy of the 'catalyst' or diluent component may be absorbed as infra-red radiation. In all that has gone before this defect has been supplied by raising the temperature, and the hypothesis cannot be considered as entirely justified unless it be proved that resolution of the complexes can be achieved by exposure to infra-red radiation. The fact that the most effective method of deactivating an activated phosphore and of releasing the whole of its phosphorescence is by exposing it to infra-red radiation adds a conclusive argument in support of the hypothesis.

The success that has attended the application of the hypothesis of complex formation to widely differing phenomena justifies its general application to all thermal chemical reactions. This naturally leads to the view that every such reaction depends on the presence of a catalyst. There seems little objection to this because it is a fact familiar to everyone that chemical reactivity suffers a most remarkable decrease as all impurities are removed. It is perhaps a sweeping statement to make that no thermal reaction can take place in the complete absence of a catalyst, but the fact remains that in every case which has been accurately examined the reaction velocity is zero. In inorganic chemistry the most effective catalyst is water, and H. B. Baker's work on the absence of reaction between dry substances is classical. It may be that this power of water is connected with its great ionising power towards inorganic salts, for it is possible that ionisation itself is the result of a complex between solvent and solute.

It may be claimed that the evidence brought forward from the three fields of photoluminescence, absorption spectra, and chemical reaction constitute a story that is not without interest. The one dominating influence in this story is the critical quantum of activation which has found its experimental verification.