THE RADIATION HYPOTHESIS OF CHEMICAL REACTION

FARRINGTON DANIELS

Laboratory of Physical Chemistry, University of Wisconsin, Madison

Few hypotheses in science have suffered such a rapid rise and fall as the radiation hypothesis. Attracting attention soon after the close of the war, it was eagerly taken up by theoretical chemists because it offered a new point of attack for an important problem which had hitherto defied solution. In contrast with the remarkable successes of thermodynamics in determining how far a chemical reaction can go, nothing but failure had come from attempts to predict how fast it will go. Any hint, however slight, was worth following in this attempt to solve the problem of reaction velocities. The radiation hypothesis seemed particularly important because it suggested a correlation between the fields of chemical kinetics, photochemistry and atomic structure,—between reaction rates, absorption spectra and activated molecules.

The names of Trautz (1), Perrin (2) and W. C. McC. Lewis (3) are associated with the development of the original radiation hypothesis. The best statements of the hypothesis were given at a symposium held in 1922 (4). Already vital objections had been raised and at a similar symposium (5) on photochemistry three years later there was little support for the remnants of the original hypothesis. Several good reviews of the hypothesis are available for work up to 1923 (6).

Experimental evidence for testing the hypothesis was lacking at first because very few reactions exist which do not have complicating phenomena such as molecular collision or catalytic effects, which mask the fundamental process. The experiments which have been devised recently to test the hypothesis have shown the original hypothesis to be untenable, and leave one which is so difficult as to defy immediate experimental proof and so complicated as to be of doubtful value if proved to be correct.

The experimental tests of the radiation hypothesis have been concerned chiefly with unimolecular reactions, because such reactions were supposed to be independent of molecular collision; and with infra-red spectroscopy, because infra-red radiation is the most abundant at ordinary temperatures, and because quantum calculations indicated that it was the effective radiation for most reactions which proceed with measureable velocity.

THE STATEMENT OF THE HYPOTHESIS

In spite of the apparent failure of the original hypothesis, certain things of importance have been brought out by its formulation. It is necessary first to state the hypothesis in its broadest terms, and the various deductions which have been associated with it.

There are four main postulates connected with the original radiation hypothesis of chemical reaction.

First postulate. Molecules must be put into an active state before they can react chemically, and in ordinary thermal reactions this activation is brought about by radiation emitted by the walls of the containing vessel.

Second postulate. The energy per gram molecule required to activate the molecules, E, (called the critical increment) may be calculated from the temperature coefficient of the reaction rate, k, by the equation

$$\frac{d \log_e k}{dT} = \frac{E}{RT^2}$$

Third postulate. Assuming that each molecule is activated by one quantum, $h\nu$, the energy absorbed in activation is given by the expression

$$E = N\,h\nu.$$

where N is the Avogadro number (6×10^{23}), h is Planck's constant (6.57×10^{-27}) erg—seconds and ν is the frequency of light. By this equation and that of the second postulate the frequency of the activating radiation can be calculated from the temperature coefficient of the reaction rate. Conversely, too, the temperature coefficient of the reaction rate can be calculated from the frequency of the light which brings about the reaction.

Fourth postulate. The relation between chemical reaction and radiation is reversible, and radiation of the activating frequency is emitted when the reaction is reversed.

UNIMOLECULAR REACTIONS

The first postulate was suggested in 1913 by Perrin (7). He pointed out that unimolecular reactions are independent of collision, for if one doubles the volume of a gas which is decomposing unimolecularily the number of collisions will be only one-fourth as great, and yet the same number of molecules decompose per second as before. This independence of concentration is a requirement of a unimolecular reaction. Perrin reasoned that since the molecules in such a reaction are independent of collisions, they cannot get their energy of activation from collisions and they must get it from radiation emitted by the walls of the containing vessel. Obviously such a conclusion is valid only in case collision and radiation are the only possibilities and in case the exclusion of collisions is fully established.

It was not long before critical examinations and new experiments showed that true unimolecular reactions are extremely rare. One by one, the supposedly unimolecular reactions were shown to be more complicated reactions, for they were found to be catalyzed by the walls of the containing vessel or by traces of impurities. It was pointed out by Rice (8) that if there are no true unimolecular reactions there is no need to invent a theory to account for them.

For some time the decomposition of nitrogen pentoxide (9) remained the "sole survivor of the group of truly unimolecular reactions" and for a while even this reaction was in doubt. Later experiments, (10), (11), (12), however, have confirmed the true unimolecular character of the reaction. Very recently this reaction has been critically studied to determine if it involves catalysis in any way either from dust particles of phosphorus pentoxide, or moisture or other material. It has again been pronounced a truly unimolecular reaction, uncatalyzed and homogeneous (13).

The existence of unimolecular reactions has been supported by the study of several other reactions as follows: The decomposition of sulfuryl chloride (14), acetone (15), propionic aldehyde (16), di-ethyl ether (17), di-methyl ether (18), azo methane (19a, b), and by the gas phase racemization of pinene (20). All of these reactions have been shown to be unimolecular, homogeneous, gas phase reactions, although in some cases the specific reaction rate falls off at low pressures.

The fact is now fully established that unimolecular reactions do exist, and they must be explained. In the next section the collision hypotheses advanced to account for unimolecular reactions are reviewed briefly.

COLLISION HYPOTHESES

Perrin believed that the collision theory was ruled out by the fact that the reaction rate is independent of the collision rate.

Lindemann (21) suggested that there may be a time lag between activation and decomposition which would make the reaction rate appear to be independent of the number of collisions. Under these conditions the activated molecule can have its energy taken away again by collisions before it has had time to decompose. The rate of decomposition, however, would still be proportional to the concentration and the unimolecular constant would be satisfied, except at low concentrations when the time between decompositions would be of the same order as the time between collisions. It has been generally supposed, however, that decomposition is synonymous with activation in a true unimolecular reaction. A comparison of the racemization of pinene with the decomposition of nitrogen pentoxide (20), supported the view that the time between activation and decomposition is negligible at least in these two reactions.

Rodebush (22) suggested a statistical theory for unimolecular reactions according to which the dissociation of a molecule is caused by a series of collisions, fortuitously timed so as to accelerate the oscillation of some part of the molecule to the breaking point.

According to these hypotheses a break-down of the unimolecular constant is to be expected at very low pressures, so low that the period between collisions is greater than the average calculated time between the decomposition of the molecules.

Attempts were soon made to ascertain if the unimolecular rate constant remains unchanged at low pressures in accordance with these ideas. The experimental errors are seriously magnified in this region. White and Tolman (10) and Hunt and Daniels (11) found no change in the specific decomposition rate of nitrogen pentoxide. Hirst and Rideal (23) reported an *increase* of nearly four fold at very low pressures but this research was quickly checked in other laboratories and the results were not confirmed. Hibben (24) and Smith and Loomis (25) found that the specific rate of decomposition at low pressures checks exactly with that of Daniels and Johnston (9) at higher pressures. Hibben carried the measurements down to 0.002 mm. without observing any change and Smith and Loomis concluded that the results of Hirst and Rideal were complicated by the absorption of N_2O_5 by solid N_2O_4.

Although nitrogen pentoxide maintains its specific decomposition rate over a very wide range of pressures, Hinshelwood found that the specific decomposition rate of the unimolecular reactions which he has reported (15), (16), (17), (18) decreases at lower pressure, and in most cases becomes di-molecular. Rampsberger (19b) found that the specific decomposition rate of azo-methane decreases also at lower pressures. These changes in the specific decomposition rate occur, however, at pressures of a few millimeters of mercury where each molecule suffers a very great number of collisions before it undergoes decomposition, and no one has succeeded yet in studying the reaction rates at pressures so low as to make the collision frequency as slow as the expected frequency of decomposition.

J. J. Thomson (26) suggested a mechanism, based on collisions, which demanded that the presence of an inert gas should increase the decomposition rate, but this prediction has not been supported by the experiments with nitrogen pentoxide (10), (11), (12). Hinshelwood (18), found that the decomposition of propionic aldehyde, di-methyl ether, and di-ethyl ether is accelerated by hydrogen but the reaction appears to be connected with some specific property of hydrogen.

The fact that the specific reaction rate of a unimolecular reaction is independent of concentration, constituted only a questionable argument against the collision hypothesis. A stronger argument against the hypothesis was based on the fact that ordinary collisions cannot supply energy rapidly enough to bring about the decomposition.

These calculations have been made by Christiansen and Kramers (27) by Lewis and Smith (28) and by Tolman (29) and all are agreed that the most natural source of energy, the collision between two ordinary molecules is insufficient to cause decomposition in a unimolecular reaction. The numbers of collisions can be calculated from the kinetic theory of gases with reasonable estimates of the diameters of the molecules. The number of collisions giving *sufficient* energy for the reaction is of the order of one-ten thousandth of the number required to check with the experimentally determined constant.

INTERNAL ENERGY OF MOLECULES

Failing to explain unimolecular reactions by ordinary collisions, workers in this field have now turned to other sources of energy. Lewis and Smith (28) suggested that the large heat capacity of the molecule of nitrogen pentoxide may contribute some energy from previous collisions.

Hinshelwood (30) pointed out that as far as our evidence goes now it is only the complicated molecules with many degrees of freedom which have been found to decompose according to a unimolecular reaction, and this observation led him to the suggestion that the internal energy of the molecule can contribute to the energy of decomposition. Since it is necessary to combine a collision of high energy with an internal arrangement of high energy (or low stability) in order to bring about decomposition, the effect of collisions is largely masked. Hinshelwood suggested also that the unimolecular decomposition may demand the liberation of free atoms, and this process requires the absorption of a large amount of energy. Only the complicated molecules with many degrees of freedom can supply sufficient energy.

Several attempts have been made to formulate quantitative expressions for the unimolecular reaction based on more elaborate collision hypotheses. In general these elaborated hypotheses make use of the internal energy of the molecule and several degrees of freedom. Roy (31) emphasized the similarity between photoelectric phenomena and photo-chemical reactions and proposed an equation for a unimolecular reaction which involved the molecular weight, the heat of dissociation, the cross section of the reacting molecule and an arbitrary constant connected with the number of valence bands.

Christiansen (32) criticized some of the deductions of Lewis and Smith (28) but emphasized the need for considering several degrees of freedom.

J. J. Thomson (33) proposed a theory for unimolecular reactions based on the assumption that the law of the conservation of energy applies as a statistical average to a group of molecules, but that it does not apply to isolated molecules if the forces inside the molecule are discontinuous. This theory led to an expression which gives an increase in the specific reaction rate at low pressures and checked the experiments of Hirst and Rideal (23) but these experiments were not confirmed (24), (25).

Fowler and Rideal (34) in a comprehensive treatment discussed the ways in which molecules can be activated by collision with sufficient rapidity. They assumed that the energies of two colliding molecules can be used. Assuming 15 degrees of freedom in the nitrogen pentoxide molecule they showed that it is possible to account for the observed decomposition rate and in fact their calculations give a rate twenty times too large. They pointed out that the target area of a molecule for de-activation may not be the same as the target area for activation.

Hinshelwood (35) and Hinshelwood and Askey (36) found that the decompositions of propionic aldehyde, di-methyl ether and di-ethyl ether were unimolecular at higher pressures but at pressures of a few millimeters they became dimolecular. The addition of hydrogen caused the unimolecular decomposition rate to be maintained down to the low pressures but helium and nitrogen did not have this effect. The authors give the name "quasi-unimolecular" to reactions which give unimolecular constants at higher pressures maintained, apparently, by collisions. They give a correction term for calculating the energy of activation, based on the number of degrees of freedom.

Rice and Rampsberger (37) suggested two theories based on the falling off of the unimolecular constant of propionic aldehyde at low pressures and the utilization of the internal degrees of freedom of complex molecules. The first theory assumes a minimum value of energy necessary for reaction and the second theory a minimum value *in a particular degree of freedom,* and each one fitted the experimental data about equally well.

Final judgment of these various hypotheses must await further experimental tests but at present it seems quite probable that unimolecular reactions can be explained satisfactorily on the basis of collisions combined with several degrees of freedom inside the molecule. More unimolecular reactions are needed as well as specific heat measurements and data from which the diameters of the molecules can be calculated. In the simpler molecules there is no time lag between activation and reaction but in the more complex molecules with several degrees of freedom the activated molecule may suffer many de-activating collisions before it has time to react. In the former case a dimolecular reaction, dependent on collision, is the result. In the latter case the time lag obliterates any apparent relation between collision frequency and rate of reaction although the collisions still provide the necessary energy. The number of molecules which reach the state, necessary for decomposition, is proportional to the total number present and thus the mathematical requirements of the unimolecular reaction are met.

Certainly these collision hypotheses are sufficiently promising so that it is not necessary to bring in radiation as an activating mechanism for these reactions.

CHAIN REACTIONS

In the preceding discussion only collisions between ordinary molecules, have been considered. Another promising source of energy which might be used to bring about the unimolecular reactions, lies in collisions with activated molecules, the so called collisions of the second class. When a molecule is in an activated condition with a displaced electron, it is able to pass over its extra energy to other molecules with which it collides. In this way energy produced in the chemical reaction can be used over again for the activation of the molecules. In other words it may not be necessary to account for the whole energy of activation but only for the heat of reaction, which in most cases is much less.

Christiansen and Kramers (27) have developed this idea to the fullest extent. They propose specific reaction chains whereby the energy liberated by the decomposition of the activated molecule is passed on to new, reacting molecules. In this way a steady state is reached with the number decomposing, proportional to the total number of molecules.

Several objections have been raised to this mechanism. First, the decomposition of a complex molecule is usually associated with the absorption of energy rather than with the evolution of energy. In the case of the decomposition of nitrogen pentoxide, at least, the whole reaction appears to be endothermic.

Second, the presence of inert molecules might be expected to absorb the energy of activated molecules and prevent its return to the reacting molecules, thus slowing down the reaction. However, in the case of nitrogen pentoxide the reaction rate is not appreciably affected by a million fold excess of nitrogen molecules (11). Even when surrounded by an inert solvent the molecules of nitrogen pentoxide decompose at nearly the same rate (38). These objections may be somewhat discounted by the fact that the action of activated molecules is likely to be quite specific, as shown by experiments on the quenching of fluorescence.

A third argument against the chain reaction is raised by Hirst and Rideal (23), who studied the decomposition rate of nitrogen pentoxide at very low pressures. The pressure was so low that each molecular chain, if it existed, would be subjected to impacts on the wall some forty times, and one impact should be sufficient to break it. In spite of these arguments it seems reasonable that some of the energy of activation can be contributed by the products of the reaction.

Norrish (39) found that nitrogen dioxide is decomposed photochemically into nitric oxide and oxygen and Busse and Daniels (40) found that nitric oxide reacts immediately with nitrogen pentoxide. These facts suggest that in the thermal reaction half of the nitrogen pentoxide molecules decompose spontaneously according to a slow unimolecular reaction but that for each molecule decomposed a second molecule of nitrogen pentoxide is decomposed by the reaction products. In this way it is possible to avoid an equation for the reaction which involves the unlikely liberation of atomic oxygen, and yet permits the equation to be written with a single molecule of nitrogen pentoxide decomposing in accordance with the experimentally established unimolecular decomposition (40). The arguments for this mechanism seem sufficiently strong to emphasize the hypothesis that some of the energy for decomposition of the nitrogen pentoxide may be obtained by reaction between the decomposition product (nitric oxide) and half of the original nitrogen pentoxide, as proposed originally by Christiansen and Kramers (27). It is probably significant that most of the unimolecular reactions fall off at low pressures except nitrogen pentoxide, and in this decomposition there is this evidence for a secondary reaction. It will be necessary to study further the thermochemistry of the nitrogen oxides before settling the question definitely.

ACTIVATED MOLECULES

At the present writing the existence of unimolecular reactions does not seem to demand activation by radiation, but it does appear to demand some kind of an activated molecule. The chief argument for the existence of activated molecules is the fact of slow reactions, for reactions should take place instantly if all molecules are equally active.

Arrhenius (41) first postulated active and passive molecules to account for the fact that a slow chemical reaction increases 20 or 30 per cent per degree rise in temperature. A shift in the equilibrium from passive to active molecules could then explain the large temperature coefficient of chemical reaction.

There has been no direct experimental proof of the existence of activated molecules in ordinary thermal chemical reactions except perhaps the spectral evidence of decomposing ozone pointed out by Wulf (42) and the influence of water vapor in quenching the infra-red emission spectrum of explosions discussed by David (43). The argument of Arrhenius based on the large temperature coefficient of chemical reactions can probably be explained with the help of statistical mechanics without the necessity of considering radiation.

On the other hand the conception of activated molecules has received a tremendous impetus through the development of the Bohr theory, for it is now easy to visualize an activated molecule, as a molecule with a displaced electronic orbit. It is probable that activated molecules may be considered best in a statistical sense with transitory displaced orbits, rather than new and stable molecules in the sense of structural organic chemistry.

THE CRITICAL INCREMENT

According to the second postulate of the radiation hypothesis it is possible to calculate from the temperature coefficient of the reaction rate, k the energy, E_c, which is required to activate the molecule and prepare it for reaction. This energy is called the critical increment, but there is some difference of opinion as to its exact definition. Most workers seem to favor the definition that it is concerned with average values, and the following definition is, perhaps, the most comprehensive. According to Tolman (44)

$$\frac{d\ ln\ k}{dT} = \frac{E_{(\text{activated})} - E_{(\text{average})}}{RT^2} = \frac{E_c}{RT^2}$$

where E is a term which contains the energy of the molecules and also the energy of the "modes of vibration" entering the reaction. R is the molar gas constant and T is the absolute temperature.

This equation seems to rest on a firm theoretical foundation. It was derived on the basis of statistical mechanics by Marcelin, (45), by Rice (46) and by Tolman (44). It is based on Maxwell's distribution law, and Hamilton's equations of motion. In Tolman's derivation the influence of radiation is considered.

Only a few experimental data are available for testing this equation directly. These tests, though, as far as they go seem fairly satisfactory.

Perhaps the most striking support for its validity involves the equation

$$k = S\, e^{\frac{-E}{RT}}.$$

In this equation k is the specific reaction rate, E is the critical increment, R is the gas constant and T is the absolute temperature. $e^{\frac{-E}{RT}}$ represents the fraction of the molecules which have sufficient energy to become activated. E is calculated by integrating the expression given earlier in this section. Experimentally, then, E may be determined from a knowledge of k at two different temperatures. Now in dimolecular reactions, S turns out to be numerically equal to the number of collisions as calculated from the classical formulas of the kinetic theory of gases and this equality could hardly be possible unless the calculation of E is correct. Also the ratio, $\frac{E}{T}$, is constant for widely different reactions, and this constancy could not be expected unless there is something significant about the calculation of E. Even in unimolecular reactions where the significance of S is not now apparent, $\frac{E}{T}$ is constant. For example (47), nitrogen pentoxide, at 55°C. gives $k = 0.00015$ and $E = 24{,}700$, and acetone at 562°C. gives $k = 0.00015$ and $E = 68{,}500$. For nitrogen pentoxide $\frac{E}{RT} = 38$ and for acetone $\frac{E}{RT} = 41$, when the temperatures are chosen so as to give equal reaction rates, i.e. the same value of k.

Another check on the calculation of E is possible through the relation between the equilibrium constant, K, and the specific reaction rates, k_1 and k_2, of the two opposing reactions, as given by the equation

$$K = \frac{k_1}{k_2}$$

According to the familiar van't Hoff equation, the heat of reaction, Q, and the equilibrium constant, K, are related as follows,

$$\frac{d \ln K}{dT} = \frac{Q}{RT^2}$$

combining this equation with the equation involving the critical increment it can be shown that $Q = E_1 - E_2$. In other words, the heat of reaction, calorimetrically measured, is equal to the difference between the energy of activation of the direct reaction and the reverse reaction. Indirect confirmations of this relation have been pointed out by Dushman (48). It would be very desirable to check this relation in significant reactions in which the temperature coefficient of the two opposing reactions, and the heat of reaction are all determined experimentally under the same conditions.

A third method for testing the validity of calculations of the critical increment is found in quantitative photochemical investigations. The photochemical energy required to cause the reaction of a gram molecule of material should check with the energy of the critical increment if secondary reactions are eliminated.[1]

THE QUANTUM HYPOTHESIS

According to the third postulate of the radiation hypothesis, given earlier,

$$E = N h\nu.$$

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[1] The results of such an experiment on nitrogen pentoxide will be reported in a later publication.

This equation involves the quantum theory and it must stand or fall with this theory. It will be noted that this equation is identical with the Einstein law of photochemistry, which seems to be gaining slightly in significance as reactions free from complications are found and experimental technique is improved.

This postulate is the one which has been most often discussed in connection with the radiation hypothesis and it was the one which first discredited the hypothesis.

The temperature coefficient. It was pointed out first that this equation leads to the requirement that a single wave length of light is effective in bringing about the activation of the molecules. Perrin (2) next showed that the temperature coefficient of the emission of monochromatic light by a black body is of the same form as the temperature coefficient of the rate of a chemical reaction. In both cases a straight line results when the logarithm of the property is plotted against the reciprocal of the absolute temperature. Perrin used this fact as an argument that reaction rate depends on absorption of radiation from the walls of the containing vessel, but Langmuir (49) showed that there is nothing significant about it, because both are probability phenomena and both follow an exponential equation.

According to this relation E should be independent of temperature. In some cases, E does change slightly with temperature but Tolman (44) used this fact as an argument for several frequencies rather than the single frequency, ν.

Originally the large difference between the temperature coefficient of reaction rate and collision frequency was considered an argument against the collision theory and therefore an argument in favor of the radiation hypothesis. However, this argument fails when it is realized that only one collision in many millions can give sufficient energy for the activation, and this frequency of unusually violent collisions is, by Maxwell's distribution law, an exponential function.

Insufficient radiation density. Against this quantum equation Langmuir (49) also raised the objection that the monochromatic radiation density is by no means sufficient to supply the energy demanded by the critical increment. Similar calculations have been made also by several others (27), (28), (29) and there seems to be no doubt that the walls of the containing vessel fall short of giving the necessary radiation by at least a million fold, when calculations are based on the black body radiation laws.

Several ways out of this difficulty have been proposed, but they are not at present convincing.

Tolman (50) proposed an elaborated radiation hypothesis in which the reacting material is activated by several frequencies instead of by one. In this way more radiant energy from the walls can be used.

It must be confessed that we know very little about the radiation *inside* a "hohraum," for all our experience is based on phenomena in which the radiation comes outside. Under the conditions of the chemical reaction the inside of the chamber is practically absolute zero as regards the radiation of the absorbable frequencies and yet it is up to full radiation temperature as regards the remaining spectrum. Under these conditions it is, perhaps, unsafe to use the classical laws of black body radiation in the ordinary way.

In view of our ignorance of radiation inside a chemically reacting system, Lewis and McKeown (51) have suggested that it is possible to draw off energy of a single frequency at very much greater rates than calculated by the ordinary radiation laws. In fact they suggested that the energy for all the other frequencies can be converted instantly into the one which is being used up and that the total radiation of the black body is available for chemical reactions.

In discussing the properties of radiation in a chemically reacting system it is necessary to distinguish clearly between a thermal and a photochemical reaction. It has been pointed out (51), (52), (31) that in a photochemical reaction the radiant energy comes from an outside source and is not in equilibrium with the system. In a thermal reaction, however, the radiation is in thermal equilibrium with the walls of the containing vessel.

The difficulty of finding sufficient radiation density may be removed in a third way, by considering that part of the energy of activation is provided by collisions, or by secondary reactions.

In this way it is conceivable that the radiation would have to supply energy corresponding to only a fraction of the critical increment. If the heat of the reaction, i.e. the difference between the critical increments of the products and the reacting material determines the energy requirement, this difficulty of insufficient radiation density can be minimized or nullified. The help offered by this consideration can be used for the collision hypothesis as well as for the radiation hypothesis.

Absorption spectra. A strong objection to the quantum postulate of the simple radiation theory is found in the evidence of absorption spectra. In many cases there is no absorption at the frequency, ν, demanded by the equation $E = N h\nu$. The most striking example is the case of nitrogen pentoxide which is a true unimolecular reaction with a critical increment of 24,700 calories well confirmed by different workers. Setting $E = N h\nu$, the activating frequency ν is in the near infra-red at 1.16μ but no absorption of light can be found in this region (52). Other examples of a similar nature can be cited.

The difficulty can be met by Tolman's elaborated radiation hypothesis (50) in which several frequencies are involved.

This quantum relation can be tested also in another way. Nitrogen pentoxide decomposes in different solvents at rates which are only slightly different than those in the gas phase. The critical increment varies slightly for different solvents and should lead to a corresponding shift in the lines of the absorption spectrum. No such shift was found (53) although the calculated shift should have been large enough to measure with certainty.

It is possible that some of the failures to check the calculated frequency, with the absorption spectrum, may be due to a confusion of several critical increments. If the experimentally determined reaction rates on which the calculation of E and ν depend, consist of several different reaction rates, the calculated frequency ν is not significant. If side reactions and consecutive reactions cannot be separated from the main reaction there is little hope of calculating the significant critical increment. This situation has been emphasized particularly by Garner (54).

Photochemical inactivity of infra-red radiation. The greatest objection to the simple radiation hypothesis lies in the fact that the calculated frequency of radiation is not able to bring about the reaction, photochemically. If this radiation, brought in from an outside source of great intensity, is inactive, then the radiation from the containing walls at a much lower temperature should not be effective.

The nitrogen pentoxide reaction again furnishes the best experimental data now available. As pointed out in the preceding section, the simple radiation hypothesis, demands that light of 1.16μ should decompose nitrogen pentoxide. Experimental facts (52), (58) show that no decomposition is effected even by very intense light of this frequency.

Although there is no absorption band at 1.16μ there are a few absorption bands in the infra-red and one of these falls at $3 \times 1.16\mu$ and another at $5 \times 1.16\mu$ (55), (53). It was thought that this fact might be significant (56) and that radiation of these wave lengths would be effective. It was shown, however, that these radiations are also inactive (57), (58). These multiples of the calculated wave length then appear as coincidences. Intense radiation from a Nernst glower was passed through a transparent bulb containing nitrogen pentoxide and it was shown that at least 99 per cent of the energy actually absorbed was without effect on the decomposition of the nitrogen pentoxide (58).

In the same research it was found that intense infra-red radiation does not decompose carbon dioxide nor hydrochloric acid gas and does not bring about the reaction between alcohol vapor and oxygen. If the radiant energy actually absorbed is divided by a very large, assumed critical increment, the quotient corresponds to thousands of micromoles, whereas the tests were sensitive to one micromole and less.

These experiments were concerned with the near infra-red from 2μ to 7μ, and Lewis and Mayer (73) have found recently that far infra-red radiation as well as the near infra-red is ineffective in decomposing nitrogen pentoxide. Hibben (24) found that infra-red radiation is ineffective also in decomposing ozone and nitric oxide. Although the cases now available for test are too few for extensive generalization, there is up to the present time no established case of a chemical reaction brought about by infra-red radiation, except possibly the influence of infra-red radiation on explosions (43). This situation is to be expected for,

> According to present theories absorption bands in the near infra-red are due to the displacement of atoms within the molecule, while visible and ultra-violet absorption lines are due to the displacement of electrons. The latter process results frequently in chemical decomposition, but there is no evidence that the former does. It is suggested that the two processes are fundamentally different in mechanism and that atoms may be loosened in a molecule by displacement of the electrons which hold them together, but not by direct displacement of the atoms (58).

Apparently the infra-red radiation does not contain sufficiently large enough quanta, i.e. high frequency to cause activation.

When a reaction is already taking place thermally, infra-red radiation can cause slight acceleration of the reaction rate but this effect then becomes indistinguishable from an ordinary thermal effect. This phenomenon was noted in the experiments with nitrogen pentoxide at room temperatures (58).

The apparent inactivity of infra-red radiation is a serious blow to the radiation hypothesis for it was to the infra-red radiation from the walls of the containing vessel that most of the importance was attached.

THE ELABORATED RADIATION HYPOTHESIS

Although the simple radiation hypothesis has been proved untenable, it is still possible that an elaborated radiation hypothesis may survive.

Such an elaborated hypothesis has been nicely developed by Tolman (59) who discusses the following possibilities.

Simultaneous absorption of several quanta. If several quanta are involved in the passage from the normal to the activated state, the frequency of the activating light cannot be calculated by setting the critical increment equal to $Nh\nu$, because several frequencies are involved. Perrin has advanced this explanation to explain some of the failures of the simple radiation hypothesis.

This suggestion seems unlikely because coupled absorption of this type is not to be expected from the quantum theory and it is not supported by spectroscopic evidence. Moreover the chance for simultaneous collisions with two or more quanta is much less than the chance for collision with one.

Successive absorption of quanta. It is quite possible that the molecule does not pass from a normal to an activated molecule in a single change, but rather that it passes through a series of intermediate stages. Several smaller quanta of different frequencies would then be required and the discrepancy between calculated and observed absorption bands could be explained. This mechanism, however, is of no help in getting around the difficulty of insufficient radiation density.

Simultaneous absorption and emission of quanta. If quanta are emitted simultaneously with the absorption of quanta the radiation in a closed space may suffice to give reaction rates which agree with those experimentally determined, but there is no evidence now to show that this process is important.

Absorption of a range of frequencies. Instead of a single activated state, there may be a whole range of activated states of continuously increasing energy content. Such an increase in the number of activated states would help greatly in the problem of obtaining sufficient energy to account for the observed reaction rate, but it is not possible now to test the hypothesis quantitatively. This modification of the simple radiation hypothesis appears to be the least hopeless.

Another way out of the difficulty may possibly be found in the suggestion of Polanyi (60) that a coupling through radiation exists between the molecules decomposing and those being activated.

THE EMISSION OF LIGHT

According to the fourth postulate of the radiation hypothesis, radiation of the activating frequency is emitted when the reaction is reversed. The idea can best be illustrated with a specific case.

It has been found experimentally that light of 180 $m\mu$ will convert oxygen into ozone and that light of 280 $m\mu$ will convert ozone into oxygen, according to the reactions,

$$180\ m\mu + 3O_2 \longrightarrow 2O_3$$

and

$$3O_2 \longleftarrow 2O_3 + 280\ m\mu$$

These two equations may be considered together and written as an ordinary balanced reaction

$$180\ m\mu + 3O_2 \rightleftarrows 2O_3 + 280\ m\mu$$

The reversibility of such a process seems perfectly natural. If the complete reversibility is correct, it follows that light of 280 $m\mu$ is emitted when ozone is formed, and light of 180 $m\mu$ is emitted when ozone is decomposed.

In general

$$N\ h\nu + A \rightleftarrows A' + Nh\nu_1$$

where ν and ν_1, are different frequencies, and A and A' are the reactants and the products. Similar equations would apply also to polymolecular reactions.

Perrin (2) and Lewis (3) have pointed out how simply this hypothesis will explain the phenomena of chemiluminescence, fluorescence and phosphorescence. The emission of light is, in fact, a necessary requirement of chemical reaction and fluorescence is simply a special case in which the chemical reaction is brought about by radiation from an outside source. Phosphorescence is similar to fluorescence except that a time lag is involved in the chemical reaction. There is something very attractive about this fourth postulate of the radiation hypothesis.

According to the original radiation hypothesis all chemical action is accompanied by the absorption of radiation and all chemical reaction involves the emission of radiation. Indeed, it is strange that chemiluminescent reactions are not more common. If the absorption of radiation, however, is not a necessary precursor for chemical reaction, then the simple radiation hypothesis falls and the emission of light is not a necessary accompaniment of chemical reaction.

It must be pointed out that the experimental tests for this emission of light are difficult. The light intensity is very low in slow reactions and only the light emitted near the outside of the reacting mass can be detected. Most of the light is emitted in the interior, where it is absorbed by the molecules of the products before it can get out. Possibly the quantity of light reaching the outside of the reacting system is too small to be detected except in special cases where the absorption coefficients happen to be favorable.

Although several examples of chemiluminescence are known in no case has the frequency of the emitted light been connected quantitatively with the radiation hypothesis.

It is worth while to search for new examples of chemiluminescence in simple reactions where the critical increment can be determined. Also, a study of the temperature coefficients of rates of luminescent reactions may give information concerning the critical increment of luminescent reactions, which are now known. Two tests of the quantum equation are possible as shown by the following equations

$$\text{Frequency of emitted light, } \nu, = \frac{E}{Nh}$$

and

$$\text{Heat of reaction, } Q, = E_1 - E_2 = Nh(\nu_1 - \nu_2)$$

According to the latter equation the difference in the frequency of the emitted light and that of the chemically activating light multiplied by *Nh*, is equal to the heat of the reaction. The latter test avoids the necessity of determining the critical increments. Direct experimental tests of these equations are lacking at present.

Perrin (61) has studied the fluorescence of dyes, particularly methylene blue in glycerin in an attempt to check relations predicted by the radiation hypothesis. In general, there seems to be some indirect evidence supporting the radiation hypothesis.

Some experiments have seemed to confirm the predictions of the radiation hypothesis but they have been later disqualified. A case in point is concerned with the absorption spectrum of anthracene and the prediction of certain quantum relations (62), but the absorption bands on which the predictions were based were later shown to be due to impurities (63).

Great care must be exercised in experiments designed to test photographically the emission of light in chemical reactions, for photographic plates are very sensitive to organic vapors and other substances. For example it was reported by Kugelmass and McQuarrie (64) that ultra-violet light is emitted when cod liver oil is oxidized and that oxygen is liberated when the oil is radiated with ultraviolet-light. These experiments were of interest in the study of the cure of rickets and they appeared to constitute an excellent example of the fourth postulate of the radiation hypothesis. The results were not checked (66) however, and the first conclusions were withdrawn (65).

The question to be decided by future experiments is whether radiation is usually emitted in chemical reactions but in such a way that it cannot be easily detected; or whether the energy evolved in a chemical reaction goes immediately into kinetic energy of the molecules.

EXPLOSIONS

Important facts bearing on the question just raised have been discovered in the study of explosions. Light is emitted in flames and explosions and it has been known for some time that a considerable quantity of infra-red radiation is emitted. These are violent, rapid reactions and here if anywhere the emission of radiation should be sufficiently great to detect. The fact that radiation is emitted in these reactions, constitutes a support for the radiation hypothesis.

The question arises as to whether this emission of radiation is really chemiluminescence or whether it is thermal emission. In the first place we know very little concerning the emission of radiation from a heated gas in the absence of chemical reactions or electrical ionization. More experimental data in this field would be very valuable.

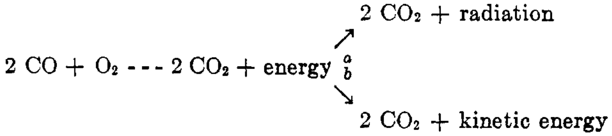
The following considerations show that some of the radiation at least is due to chemiluminescence:

1. David (67) found that the emission of radiation is greatest before the maximum temperature of the explosion is reached. If all the radiation is of thermal origin the greatest emission should come at the highest temperature. The most rapid chemical reaction occurs just before the maximum temperature is reached and it is here that the emission of radiation is the greatest.

2. Haslam, Lovell and Huneman (68) discovered that the preheating of the gases decreases the emission of radiation. If the radiation is due to temperature, the preheating should have increased the radiation. If the radiation is of chemical origin the preheating might decrease the emission by causing a more rapid attainment of equilibrium with a quicker degradation of chemical energy into kinetic energy.

Bone and Webster (69), found that water vapor decreases the radiation by catalyzing the reaction. Garner and Johnson (70) found that the drying of the gases decreased the temperature of the explosion and increased the emission of radiation. The possibility that water vapor acted as a screen for the infra-red radiation was carefully considered, and the conclusion was that less radiation is emitted when the reaction proceeds rapidly and allows the energy of the reaction to be dissipated as heat in molecular collisions. This view is further strengthened by the fact that negative catalysts such as carbon tetrachloride and nitrogen dioxide which decrease the speed of the explosion, increase the emission of infra-red radiation.

The following equation (70) seems to account satisfactorily for the data, and to strengthen the view that radiation is emitted in chemical reactions as predicted by the radiation hypothesis, if the conditions are right



$$\begin{tikzcd} & 2\,CO_2 + \text{radiation} \\ 2\,CO + O_2 \text{ - - - } 2\,CO_2 + \text{energy} \arrow[ur, "a"] \arrow[dr, "b"'] & \\ & 2\,CO_2 + \text{kinetic energy} \end{tikzcd}$$

The products of the oxidation of carbon monoxide contain extra energy from the chemical reaction and this energy may be released in two ways, as indicated by *a* and *b*. When the reaction is rapid most of the energy is converted into increased kinetic energy by collisions between these activated molecules and other molecules. When the reaction is slower and the energy is not dissipated immediately in collisions, there is an opportunity for the activated molecules to lose their energy by radiation as indicated by the reaction, *a*. In ordinary, slow, thermal reactions the reaction, *b*, must predominate greatly over the reaction, *a*.

David (43) found that infra-red radiation accelerates the rate of combustion of inflammable gases if the radiation is absorbed. Later experiments (71), however, indicated that the phenomenon is complicated by the fact that the effect was not noted in the absence of nitrogen, and that in some way the reaction involves the oxides of nitrogen.

Certainly radiation and particularly infra-red radiation is emitted in all explosions and this fact lends support to the fourth postulate of the radiation hypothesis.

RADIATION AS A FACTOR

The following hypothetical experiment (72) proves that radiation must be a factor in some chemical reactions, although probably a small factor.

A quantity of ozone is being decomposed photochemically by black-body radiation emitted from a heated enclosure. The ozone is then placed inside the heated enclosure. Certainly the decomposition caused by the radiation will now be just as rapid as before, and probably a great deal more rapid. The fact that the ozone is being decomposed with extreme rapidity by the increased kinetic energy of the heated molecules does not nullify the fact that radiation is still causing some ozone molecules to decompose and that radiation *is* a factor in the thermal decomposition.

Direct experiments (72) have shown, however, that radiation from the walls of the containing vessel is not the important cause of activation in a thermal reaction. A stream of heated air was mixed with a stream of nitrogen pentoxide gas in an open room and although the walls of the containing vessel (the room) were at too low a temperature to bring about rapid decomposition, the nitrogen pentoxide decomposed almost as soon as it came in contact with the heated molecules of air. Molecular collision rather than radiation was therefore responsible for this reaction.

Lewis and Mayer (73) found that pinene vapor is not racemized by passing it through the center of a heated tube in a uni-directional stream. This experiment constitutes another decisive argument against the radiation hypothesis because the radiation in the tube corresponded to a temperature sufficiently high to racemize the pinene immediately.

CONCLUSIONS

In conclusion it may be stated that the existence of unimolecular reactions has been fully established but that there is, as yet, no completely satisfactory explanation for their existence. According to different views expressed in the literature, unimolecular reactions cannot be caused by collisions, they cannot be caused by radiation and they cannot be caused by anything but collisions or radiation. Not one of these views can be taken as final.

The hypothesis that radiation is the important factor underlying chemical reaction was originally based on the existence of unimolecular reactions and the difficulty in explaining them on the basis of collision. This argument is not valid now, since several possible hypotheses based on collisions have been brought out by the challenge of the unimolecular reaction and the successes of the past few months in this direction suggest that still more satisfactory theories will be forthcoming. At present the most promising explanation lies in the collision hypotheses and the utilization of the internal energy of the molecule and many degrees of freedom.

The argument for the radiation hypothesis which was based on the large temperature coefficient of chemical reactions is not valid.

The calculation of the critical increment and the conception of activated molecules seem to be satisfactory and fruitful at the present time. Neither has been disproved experimentally, but on the other hand the experimental evidence in favor of them is meager.

The simple radiation hypothesis involving the quantum theory has been disproved by a number of experiments. These experiments involve (*a*) the insufficiency of radiation density in a thermal reaction; (*b*) the discrepancy between calculated and observed absorption bands; (*c*) the chemical inactivity of infrared radiation; (*d*) experiments with cold walls and heated gas, and experiments with cold gas and heated walls.

Objections to the simple radiation hypothesis may be met in several ways, although it must be emphasized that there is now no experimental backing for them.

1. An elaborated radiation hypothesis using many frequencies is possible.
2. Many objections may be removed by admitting complete ignorance of black body radiation laws when applied to chemically reacting systems.
3. The discrepancies may be attributed to complicating intermediate steps, the experimentally determined reaction rate depending on the summation of several reactions.
4. The energy requirements may be much reduced if the products can return part of their energy to the reacting materials.

The reversibility of the relation between chemical reaction and radiation has not been explored very far, and for this reason the field is particularly attractive. Here again, the majority of the evidence does not support the radiation hypothesis, but it cannot be said that this postulate of the radiation hypothesis has yet been disproved. There is something particularly appealing in this postulate, because of its "reasonableness" and because of the ease with which it explains the phenomena of chemiluminescence and fluorescence.

Finally it must be emphasized that photochemical reactions and chemiluminescence reactions do exist, and that in some reactions at least, radiation must be a factor. At present the evidence seems to indicate that radiation is not important in ordinary thermal reactions.

The radiation hypothesis, like all hypotheses, has helped in the development of science by inspiring new laboratory experiments and further generalizations, and it has exerted a considerable influence on chemical research of the past decade. It has advanced particularly the fields of chemical kinetics and infra-red radiation.

Although three of its four postulates appear to be discredited and there is little support for the fourth, the field is still an attractive one, both for theoretical speculation and experimental exploration.

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