ACTIVATION BY LIGHT AND BY COLLISIONS IN THERMAL EQUILIBRIUM

FRANCIS PERRIN

Laboratoire de Chimie Physique, Université de Paris, France

The conception of activated molecules, now well established by the quantum theory, was first introduced by Arrhenius to explain the strong thermal acceleration of chemical reactions, and the success of this theory seems to prove positively that the activation of molecules is the first step of most reactions. But we still know very little about the mechanism of these activations.

A priori, the change in the energy of a molecule during an activation or a deactivation may be produced either by some interaction with another material system (molecule, atom, or electron), or by electromagnetic radiation. (In the first case the mechanism is usually called a *collision*; but as the distance of interaction is often much larger than the diameter of the molecules, it is sometimes better to use the word *induction*.)

The possibility of producing molecular activation or deactivation by means of radiation has been greatly emphasized by the quantum theory, whose fundamental relation determines the frequency of the light which can be connected with a given energy of activation. According to this theory, except in the single case of a metastable activated state, any activation can be produced by the absorption of a photon of the required frequency, and inversely, the return of the molecule to its normal state may occur by the spontaneous emission of a photon.

In a medium in thermal equilibrium, there must exist, according to the fundamental law of statistical mechanics, a well determined proportion of activated molecules of each substance present. But as all activated molecules are essentially unstable, such molecules can exist in a permanent state only if continually new activations of ordinary molecules compensate the unavoidable deactivations of the activated molecules.

What is the origin of the energy required by these activations which occur in a medium in thermal equilibrium, for instance at room temperature, and are the first condition of any chemical reaction? Are they due to collisions between molecules, or to absorption of light borrowed from the thermal radiation? This question is very important for our knowledge of the mechanism of purely thermal reactions. (We shall not consider in this paper the thermal *chain* reactions in which most of the activations are due to the reaction itself and are not of thermal origin.)

It was at first admitted that the activations of molecules in the usual chemical reactions were due to collisions. But on this hypothesis it is difficult to explain the invariance of the rate of a gaseous monomolecular reaction when the pressure becomes very low. The only possible cause of activation is then the thermal radiation, and this is one of the reasons which led to the development of the so-called radiation hypothesis (Jean Perrin).

This radiation hypothesis had some theoretical success, but was proved to be certainly erroneous in the case of the few reactions which could be thoroughly studied. The experiments of Professor Farrington Daniels show that the thermal radiation is not the cause of the decomposition of nitrogen pentoxide. Moreover, very often there is not enough available energy in the thermal radiation to account for the reaction velocity observed. And, finally, though the coefficients of thermal acceleration of the chemical reactions which have been studied at room temperature correspond to active frequencies situated in the infra-red, no photochemical reactions have ever been observed in this region of the spectrum.

One might be inclined to conclude from these facts that the thermal radiation never takes any part in the activation of molecules at room temperature. However, this conclusion would also be erroneous. We shall see that the study of fluorescence, combined with an application of the principle of microscopic reversibility, proves that in certain cases the thermal activations of molecules are due to radiation. We shall find at the same time an important characteristic of the mechanism of activation by collision (2) (3) (4).

Any fluorescence is due to the spontaneous deactivation with emission of light of molecules which have been activated by an external illumination, increasing greatly the intensity of the active radiation. Generally the number of emitted photons is smaller than the number of absorbed photons, and this fact proves that some of the molecules activated by absorption return to their normal state, without emission of light, by a mechanism producing kinetic energy and finally heat. The light efficiency, that is to say the ratio of the number of emitted photons to the number of absorbed photons, or, which is the same thing, of the number of deactivations by emission of light to the total number of deactivations, is usually less than one, and sometimes very small.

The probability of deactivation by emission is an internal probability practically independent of the external conditions. Therefore any variation of the fluorescence efficiency is due to a variation of the probability of kinetic deactivation. Such a variation is always observed when the concentration of the fluorescent substance is increased, the fluorescence efficiency becoming very small in highly concentrated solutions. This fact proves that the probability of kinetic deactivation of an activated molecule of the fluorescent substance is very much increased by the presence in its neighborhood of an ordinary molecule of the same kind. For instance, a molecule of fluorescein, activated by absorption of light in an aqueous solution, is practically unaffected by the presence of a great number of water molecules or by collisions with these molecules, since in a very dilute solution the fluorescence efficiency is nearly equal to one, which means that the deactivation is nearly always due to emission of light. But if in the neighborhood of this activated molecule there happen to be molecules of fluorescein in their normal state, it is very probable that a kinetic deactivation will occur. It seemed very likely, by analogy with electromagnetic induction, that this sensitiveness to the presence of a molecule of the same kind, when other molecules were without any effect, was due to a resonance between the two molecules, and this hypothesis has been verified. In fact, the diminution of the fluorescence efficiency is also produced by adding to the solution any substance having an absorption band close to that of the fluorescent substance, whatever the chemical differences between the two substances (1).

In short, the study of fluorescence, especially in liquid solution, gives a direct knowledge of three mechanisms of quantum transformations: activation by absorption of light; deactivation by emission of light; and kinetic deactivation by induction between two synchronous molecules, no such deactivation being generally possible between two different molecules having no resonance relation. This last mechanism is certainly connected with the mechanism of transfer of energy between two molecules in resonance, which has been explained by the wave mechanics.

Besides these mechanisms, only one other is well known—that is, the activation by collision between a molecule (or atom) and a free electron. The activation of a molecule by collision with another molecule, which is usually supposed to be possible, is on the contrary very incompletely known, and has been observed only in rather complicated phenomena such as the luminescence of positive rays.

It seems probable that any mechanism of molecular transformation might be exactly reversed, and Klein and Rosseland have shown the necessity of this possibility. The principle of microscopic reversibility, which is an extension of the second law of thermodynamics, compels us to admit that in a medium in thermal equilibrium, reverse mechanisms of activation and deactivation exactly balance one another. It is thus possible to infer from the observed existence of a mechanism of quantum transformation, that the reverse mechanism also exists, and we are sure that in thermal equilibrium both these mechanisms will have the same importance.

For instance, the inversion of the mechanism of activation by an electronic collision, or collision of the first kind, leads to a mechanism of deactivation by collision with a slow free electron, or collision of the second kind.

Similarly, we have seen that for certain fluorescent substances, a kinetic deactivation of the activated molecules may be produced by the presence of a molecule in resonance, but not by the presence of other molecules. Therefore we are sure that an ordinary molecule of such a fluorescent substance may be activated by a collision with a molecule in resonance if there is sufficient available kinetic energy, but that it cannot be activated by collision with a molecule not in resonance with it, even if the required kinetic energy is available. For example, a molecule of fluorescein may be activated by a collision with another fluorescein molecule, but cannot be activated by collision with a water molecule, even if the kinetic energy available in both cases is the same.

We have thus found an important feature, which had not been suspected before, of the mechanism of activation by collisions. The available kinetic energy of two colliding molecules may produce an electronic activation of one of them, only if a resonance condition is satisfied.

The fact that a molecule of fluorescein in a dilute aqueous solution cannot be activated by the collisions of the surrounding water molecules, even if these collisions are sufficiently violent, makes it probable that if this molecule is activated it will be by absorption of radiation. A new application of the principle of microscopic reversibility proves that it is really so in this case, and, in general, gives for the first time a precise answer to the fundamental question of the relative importance of collisions and of radiation in the thermal activation of molecules.

Let us consider a certain substance at a given concentration and temperature,—for instance, one of the reagents in a chemical reaction going on under some well-defined conditions. We can measure the fluorescence efficiency corresponding to any state of activation of the molecules of this substance in the given conditions, by exposing the medium to an external beam of the light of the required frequency, having for this frequency a stronger intensity than the thermal radiation at the considered temperature. Let us suppose that this efficiency is one-third, i.e. among the molecules which have been activated by the external beam of light, one out of three will be deactivated by emission of light. The total probability of deactivation by emission of an activated molecule under given conditions must be independent of the cause of its activation. Therefore, even if we cease to illuminate the medium from outside, we are sure that on an average one out of three molecules of the given substance in the specified activated state, whatever be the cause of their thermal activation, will be deactivated by emission of light, the two others being deactivated by kinetic processes. *Vice versa,* the statistical equilibrium of the system requires that the reverse mechanisms of activation should have the same probabilities, that is to say, that one out of three activations should be produced by absorption of light, provided by the thermal radiation. If it were not so, the substance considered would give to the thermal radiation more energy than it borrows from it, in opposition to the precise form of the second law of thermodynamics.

In general we see that: *The relative importance of radiation in the thermal activation of the molecules of a given substance is equal to the efficiency of the corresponding fluorescence under the given conditions.*

In a dilute aqueous solution of fluorescein in thermal equilibrium in a dark room, at the ordinary temperature, the few fluorescein molecules which will pass into the activated state corresponding to the absorption band in the visible spectrum, will receive their energy from the thermal radiation; they will be activated by absorption of light. And on the contrary, in a concentrated solution of the same substance, at the same temperature, nearly all the similar activations will be due to collisions, since then the fluorescence efficiency is very small; but in this last case, the activations will be due to collisions between two fluorescein molecules, and hardly ever to a collision with a water molecule.

If, in the chemical reactions which have been so far studied, the activations of molecules are due practically only to collisions and not to the thermal radiation, it may then be concluded that the efficiencies of the fluorescences which would correspond to these activations, are nearly zero. This is not very surprising, since the substances having a good fluorescence efficiency are indeed rather exceptional. Moreover, in the known reactions the energies of activation correspond to infra-red frequencies, and no fluorescence has ever been observed in this region of the spectrum. It seems probable therefore, that in the infra-red the fluorescence efficiencies are usually very small, and this explains fully the general failure of the radiation hypothesis. But if a substance having a strong infra-red fluorescence should be found, one might expect to observe with it some thermal chemical reactions for which the activations of molecules would be due to radiation.

SUMMARY

Deactivation of activated molecules by collision is very common, but deactivation by radiation is rather rare. Deactivation by radiation has been studied through experiments on fluorescence, and it has been found that fluorescence can be quenched only by molecules which are in resonance with the activated molecules.

Applying the principle of microscopic reversibility, it may be concluded that the available energy of colliding molecules can produce electronic activation only if a condition of a resonance is satisfied.

The relative importance of radiation in the thermal activation of the molecule of a given substance is equal to the efficiency of the corresponding fluorescence under the given conditions. In most chemical reactions which have been studied thus far fluorescence is negligible, and in these cases activation by radiation is relatively unimportant.

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