PRIMARY PHOTOPHYSICAL PROCESSES

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ABSTRACT

Photochemical reactions originate from specific electronically excited states and often the direction of a photochemical transformation depends critically on the nature of the reacting state. Nevertheless, ordinary photoreactions of polyatomic molecules have ground state products and their mechanisms must, therefore, include diabatic transitions from higher to lower potential energy surfaces. The possible nature of such processes is discussed and an attempt reported to observe electronically excited products. The role of the Hellmann–Feynman theorem in photochemistry is emphasized.

I. INTRODUCTION

In our days photochemistry has found widespread interest not only among physical chemists but also with organic chemists, who have added photochemical reactions to their arsenal of synthetic methods. It might be that polymer chemists have rather mixed feelings about photochemistry. They will certainly dislike those photochemical reactions by which u.v. or even visible light breaks into parts the long molecular chains of their polymers which they have synthesized with so much effort. On the other hand, photochemical reactions have for many years been successfully used for the initiation of polymerization. Moreover, as it has turned out lately, photochemical reactions are suitable for the chain growing process itself. These positive but also the negative aspects mentioned here are certainly enough to justify this symposium.

The lecture which I am to give here is not specifically concerned with photochemistry in relation to polymers. Instead it is on aspects of photochemical reactions in general together with the physical processes to which they are intimately connected. It is mainly our increasing knowledge of these interrelations which has led to the successful applications of photochemical methods in present day preparative chemistry.

In connection with photochemical reactions, light should not be considered as just another form of energy. When a molecule absorbs a quantum of light, either from the visible or from the u.v., this not only increases its energy content but alters essentially its physical and chemical properties. The absorbing molecule is transformed into an excited electronic state, the properties of which are as well defined as those of the ground state but generally are essentially different from these. It is this difference in physical and chemical properties of electronically excited states which then results in the photochemical transformations. Photochemical reactions should be considered as reactions of molecules in their electronically excited states.

II. DEACTIVATION OF THE EXCITED MOLECULE

The matter is a little complicated by the fact that there are several excited states which, if nothing else occurs, are passed one after the other in sequence. We shall consider at first some of these states in the typical case of an organic molecule with an even number of electrons and with a singlet ground state S_0. The molecule may be considered also as a model of a monomeric unit in a polymer, e.g. the phenyl group in polystyrene, as long as the effects of an interaction between such units may be disregarded. The lower excited states can then be imagined as resulting from the promotion of one electron from the highest filled orbital into the next higher empty one. The spins of the two lone electrons may be antiparallel or parallel to each other so that singlet- and triplet-excited states result. According to Hund's rule, the lowest excited state is generally a triplet state. It is important that the higher excited states are energetically less separated from each other than they are separated from the ground state. Each of these different states has, of course, its pattern of vibrational levels extending to higher energies.

Let us now consider the fate of the molecule, which at the moment we assume to be chemically inert, after having absorbed a quantum of light (*Figure 1*). From its singlet ground state it will be transformed into an excited singlet state because triplets are practically inaccessible by direct excitation.
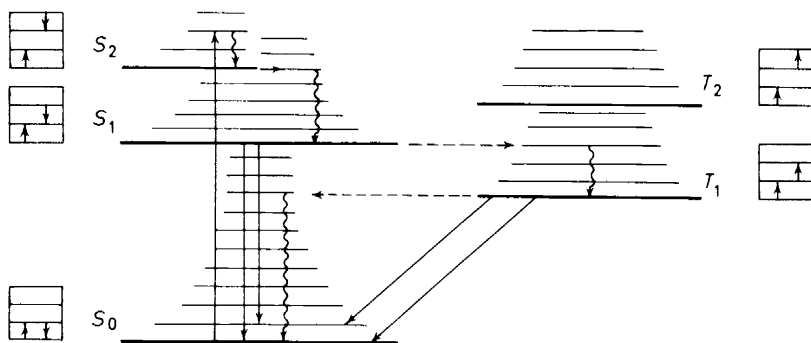

Figure 1. Excited states and transitions between them in a typical organic molecule:
→ : radiationless transitions,
⌇⌇→ : thermal equilibration,
--- → : internal conversion and radiationless interconversion.

In general, one of the higher vibrational levels of that state will become excited so that the molecule attains not only electronic but also an amount of vibrational energy in excess of that of its surroundings. It is, so to speak, a

hot molecule too. In condensed phases, which alone we consider here, this excess of vibrational energy is dissipated very rapidly, and thermal equilibrium is restored within about 10^{-12} sec. After that, the molecule is still in the same electronic state as before but in one of its lower vibrational levels. In case the excitation has led not to the first but to one of the higher excited singlet states, another fast process sets in. This is the process of internal conversion by which electronic energy is converted into vibrational energy which then again is rapidly dissipated. Between states of the same multiplicity and within the dense manifold of higher excited states this occurs as a radiationless process and takes no more than about 10^{-12} sec. Within a time interval of that order the preliminary excited state is thus transformed into the thermally equilibrated lowest singlet state S_1.

The lifetime of this state is—still in the absence of any photochemical processes—essentially longer than that of the preceding states. Internal conversion to the ground state S_0, which in principle occurs, is generally slow because of the large difference in electronic energy of both states which has to be transformed into vibrational energy[1].

Usually the lifetime of the lowest singlet state S_1 is terminated not by internal conversion but by one or the other of two different processes. One of them is the radiative fluorescence transition to the ground state $S_1 \rightarrow S_0$. The other is the radiationless intercombination $S_1 \rightsquigarrow T_1$ which—eventually via higher triplets—leads to the thermally equilibrated lowest triplet state T_1 of the molecule[2]. This process is, in principle, one of internal conversion, however, in between states of different multiplicities. As a spin-forbidden process it is several orders of magnitude slower than internal conversion between excited states of the same spin manifold. Nevertheless, it is usually faster than internal conversion to the ground state because of the much smaller energy separation of states. Fluorescence emission and radiationless interconversion together restrict the duration of the lowest excited thermally equilibrated singlet S_1 to typically 10^{-8} sec.

The lowest triplet state T_1 which is then finally arrived at lives still longer because it could convert to the singlet ground state S_0 by spin-forbidden processes only. These are phosphorescence emission and radiationless intercombination which, if present alone, might permit a lifetime of several seconds. This holds, however, for pure rigid inert solvents only because otherwise several bimolecular processes of either physical or chemical nature occur which drastically reduce the lifetime of the lowest triplet state T_1. About 10^{-3} sec might be expected in a fluid inert solvent.

The processes of thermal equilibration, internal conversion and intersystem crossing, together with the radiative processes of fluorescence and phosphorescence are the only ones which occur with a photochemically stable molecule in its inert surroundings.

If there are other molecules close to the primarily excited one, which may be chemically inert but have excited states of equal or lower energy than the first one, excitation transfer may occur on the singlet[3], or on the triplet[4] level[5]. This should be considered as a continuation of the rather physical processes by which the original energy content of the absorbing molecule is gradually diminished. In an aromatic polymer repetitive transfer may involve a large number of monomeric units.

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III. THE PRIMARY PHOTOCHEMICAL PROCESS

In addition to these processes, others of a chemical nature may occur and result in photochemical reactivity. The so-called primary photochemical process might be defined[6] as the first chemical process which takes place in addition to the rather physical processes of the deactivation cascade. It may be an intramolecular process of the absorbing molecule alone or an intermolecular process with others participating. It may involve the fission of existing bonds and/or the formation of new ones in the absorbing molecule alone or with its partner. It seems reasonable also to include electrochemical processes which include the transfer of an electron to or from the excited molecule. Excitation transfer, however, should be omitted here and preferably included into the physical processes of the deactivation cascade.

The primary photochemical process may thus occur at:
(1) the primary excited, vibrationally hot higher or first excited singlet S_n^v or S_1^v respectively;
(2) the thermally equilibrated lowest excited singlet S_1;
(3) the thermally equilibrated lowest excited triplet T_1.
In some cases, other states such as a higher triplet T_n may be passed and live long enough to transfer or to react[7, 8].

The order given here is that of sequence in time. It is likewise one of decreasing energy and of increasing lifetime. Whether the higher energy content or the longer lifetime is more essential for the reactivity of a specific excited state depends on the primary process itself. Spontaneous dissociation into radicals or isomerization of a small molecule should depend essentially on the available energy and occur preferentially at a hot singlet before it cools off. On the other hand, bimolecular reactions with a second partner present in solution require the reactants to come together by a comparatively slow diffusional process. The longer lifetime of S_1 or the even longer one of T_1 should then be decisive.

Much effort has been made in modern photochemistry to find out which specific excited state is the actually reacting one. Conventional flash spectroscopy[9, 10], laser flash spectroscopy[11, 12], and even the more modest methods of parallel investigations on quenching of fluorescence have proved to be valuable tools for this purpose.

It should be mentioned that an inherent difference in reactivity between singlets and triplets, other than that resulting from the difference in lifetime, does not seem to exist. Very often, however, S_1 and T_1 have different orbital configurations and this might cause an essential difference in reactivity.

One of the most important differences in photo-reactivity of unsaturated and aromatic molecules is that between π–$\pi^\star$ and n–$\pi^\star$ states. In a π–$\pi^\star$ state, either singlet or triplet, one electron is promoted from the highest filled π orbital of the conjugated system to the lowest empty $\pi^\star$ orbital. The excited molecule has then one electron in an energy-rich orbital but has also a hole in an orbital of fairly low energy. It is thus both an oxidizing and a reducing agent and may react in one or the other way depending on the properties of an available reaction partner. However, the excess electron as well as the hole are in π orbitals which are delocalized over the conjugated system. Even if the overall electronic distribution in the excited state should differ

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from that of the ground state, the reactivity is not specifically localized at a single atom and is more likely to result in the release or uptake of an electron from or by the conjugated system.

In carbonyls, nitrogen-heterocycles and many other molecules there are electrons in non-bonding orbitals which are localized at specific atoms of the conjugated system. They give rise to $n-\pi^\star$ states in which one electron has been promoted from its non-bonding localized orbital to an unfilled $\pi^\star$ orbital of the conjugated system. In such an $n-\pi^\star$ state, be it singlet or triplet, the oxidizing power is essentially localized at the atom with the half-filled n orbital. It may be better called dehydrogenizing power because it results mostly in the uptake of a hydrogen atom from a suitable reaction partner there. This occurs as the primary photochemical process in many molecules which have lowest excited singlet or triplet of $n-\pi^\star$ orbital character. There are many examples of drastic alterations in photochemical activity by substitution or even a change of solvent which are due to a change in the order of n $\pi^\star$ and $\pi-\pi^\star$ states.

IV. DIABATIC AND ADIABATIC PROCESSES

This and many other examples demonstrate that the course of a photochemical reaction depends on and is determined by the electronic properties of the reacting excited state. We usually describe ground state reactivity by means of potential energy diagrams and may do the same with excited state reactivity. Of two possible reaction paths a ground state molecule in a thermal reaction will take that of the lower activation energy. In an excited state reaction we should expect that the reaction will prefer that path which has the lowest activation barrier on the potential energy surface of the specifically excited state (*Figure 2*).
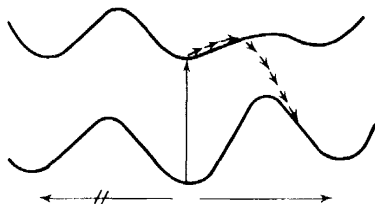

Figure 2. Potential energy surfaces and photochemical reaction.

Excited state reactions differ, however, from ground state reactions in two respects. First, for reactions of the thermally equilibrated states at least, only very low activation barriers may permit reactivity because of the short lifetimes of the states. Secondly, most common photochemical reactions do not lead to electronically excited but to ground state product molecules. Since potential energy surfaces generally do not intersect each other there

must be transitions from the upper to the ground state surfaces in between the geometrical configurations of reactant and product molecules[13]. Or, in more sophisticated language: A photochemical reaction of the common type does not proceed adiabatically in the excited state potential but is essentially a diabatic process[14].
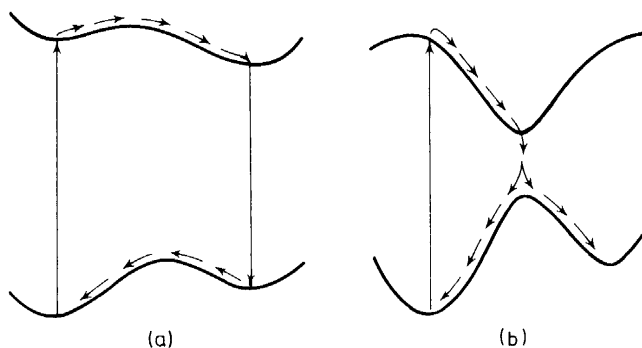

Figure 3. Pathways of photochemical reactions: (a) adiabatic, (b) diabatic.

There are, however, less common photochemical reactions which do proceed adiabatically from the reactant to the product configuration and which lead to electronically excited products [Figure 3(a)][15]. Most of them are proton transfer reactions. Their products are recognized in the excited states by fluorescence emission if these are singlets or by flash spectroscopy in the case of triplets. All reactions of that sort are reversible insofar as, following deactivation, very fast reverse reactions drive the systems back to the original composition so that no permanent chemical change occurs. It follows from the condition of adiabaticity together with that of a low activation barrier in the excited state that the ground state activation barrier has to be low too. The fast reversibility is, thus, a consequence of adiabaticity.

In an ordinary photochemical reaction the potential energy surfaces are essentially different[6, 16] [Figure 3(b)]. In the ground state, reactant and product configuration are separated by an activation barrier which is high enough to make the ground state reaction slow. The excited state potential is usually unstable at the reactant side and a negative gradient drives the system off its original configuration along a reaction coordinate in the direction of a minimum at a configuration between those of reactant and product.

In a configuration like this, radiationless deactivation is fast because of the essential difference in curvature of ground and excited state potentials and because of the smaller separation in energy. Depending on the location of the minimum the probability of the system to arrive finally at the reactant configuration should be smaller or larger and so also the quantum yield of the primary process. It is obvious that a diabatic course only allows an

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appreciable ground state activation barrier to be overcome and thus provides the driving force in a photochemical reaction.

Potential energy diagrams like this should be appropriate for intra-molecular photorearrangements such as *cis–trans* isomerizations, cyclizations and ring-openings which occur as electrocyclic reactions in the meaning of Woodward's and Hoffmann's rules[17].

For a few cases the qualitative features of the potentials depicted here have been corroborated by quantum chemical calculations[18–20]. Minor deviations from them may certainly exist. So, in some cases the excited state potential has at the reactant configuration a shallow minimum which is separated from the deeper one at an intermediate configuration by a minor barrier[21]. Or, two excited state potentials may have contact with each other in a so-called Teller crossing[22].
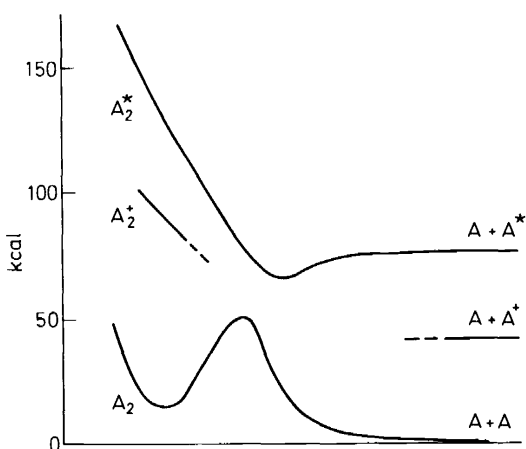

Figure 4. Dimerization of anthracene derivatives, tentative potential energy diagram.

By suitable interpretation of the reaction coordinate the diagrams might be appropriate for bimolecular primary reaction too. The specific case of bimolecular photocyclizations of aromatic molecules should, however, be considered more in detail. The diagram in *Figure 4* as an example, is intended to represent semi-quantitatively the ground and excited state potentials of the anthracene–dianthracene system[14].

The formation of dianthracene from two separate unexcited anthracene molecules is an endothermic reaction and has a considerable activation energy. The photochemical dimerization takes place between an excited and an unexcited singlet molecule. There is ample evidence that the reaction proceeds via an anthracene excimer[23–25], which should be represented here as a shallow minimum on the singlet excited state potential. From here radiationless deactivation should lead again to the ground state either of the dimer or of two separate monomer molecules.

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With some substituted anthracenes which also photodimerize, the deactivation of the excimer occurs radiatively as it does in non-photoreacting systems. The same potential energy diagram applies to the reverse photo-dissociation of dianthracene which is also an excited singlet state reaction. This too is essentially a diabatic reaction even though the conditions would seem not too unfavourable for an adiabatic course under preservation of excitation[25a].

V. THE HELLMANN–FEYNMAN THEOREM IN PHOTOCHEMISTRY

In the previous section we considered a photochemical reaction as a process beginning (but generally not ending) on the potential energy surface of a certain electronic state of the system. On this basis more or less accurate quantum chemical calculations have been performed for several photo-reactions in order to determine the reaction coordinates and to evaluate possible activation barriers. This procedure involves, of course, the cal-culation of state energies for a manifold of different nuclear configurations in between those of reactant and product. On the other hand, successful inter-pretations have been made of the pathways of possible photoreactions or of relative photoreactivities from the electronic charge distribution of the reacting state in its original geometry. One example for this is Havinga's discussion of nucleophilic photosubstitution reactions of benzene deriva-tives[26]. Similar calculations in a case of adiabatic phototransformations, namely on the photoprotonation equilibria of N-heterocycles, have been reported by Grabowska and Pakula[27]. Numerous other diabatic and adiaba-tic phototransformations have been discussed qualitatively from the elec-tronic charge distribution by purely electrostatic arguments.

There is indeed some sound basis for considerations like this. The Hellmann–Feynman theorem[28] states that the forces acting in a certain quantum state n between the nuclei of a molecular system are exactly those which according to classical electrostatics would arise from the electronic space charges in that state together with the nuclear point charges. In mathematical formulation this reads:

$$\frac{\partial E_n}{\partial Q_r} = \left\langle \psi_n \left| \frac{\partial V}{\partial Q_r} \right| \psi_n \right\rangle \tag{1}$$

Here ψ_n is the electronic wavefunction of state n, E_n is its energy, Q_r, any nuclear coordinate, and V is the potential energy of the molecular system.

In the equilibrium configuration of the ground state these forces are zero. They appear in the excited state and a potential energy gradient drives the nuclei off their original configuration (*Figure 5*). If this gradient is large enough this does not merely result in a small readjustment of the original configuration but starts a photochemical primary process.

In a case like that represented in *Figure 3*(b) the direction of the photo-chemical change should be determined essentially by the gradient of potential energy at the ground state equilibrium configuration and thus be predictable

by equation (1). In the adiabatic case of *Figure 3*(a) which might represent a photoprotonation where ground and excited state potentials do not differ much, this difference could result from a mere change in the linear terms so that equation (1) might be applied to the whole region between reactant and product configurations and be used for the calculation of the shift in equilibrium resulting from excitation.
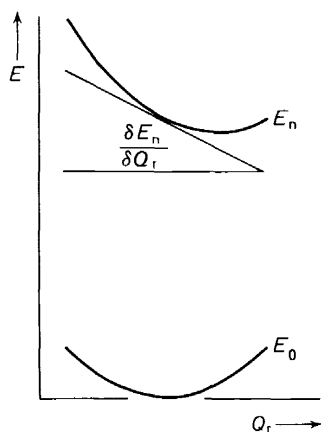

Figure 5. Hellmann–Feynman theorem in photochemistry.

Here the Hellmann–Feynman theorem seems to provide a sound justification to those predictions of photochemical pathways which are based on considerations of electrostatic forces appearing in the excited electronic state of the reactant. This is true, however, only in those cases where the first derivative of the potential determines the shift in nuclear equilibrium on the excited state potential energy surface. In other cases the second or even higher derivatives might be important too, and for these the Hellmann–Feynman theorem does not lead to a simple expression comparable to that in equation (1). Typical cases are those in which the potential energy has a saddle point and is a maximum with respect to one coordinate. The reaction would then follow this coordinate even though the gradient at the reactant configuration is zero. This will occur in more symmetrical systems like that of the disrotatory path in the often discussed photoisomerization of 1,3-butadiene into cyclobutene [17, 21]. One should, therefore, not overestimate the usefulness of the Hellmann–Feynman theorem in photochemistry.

The title of this lecture has been: Primary Photophysical Processes. Nevertheless I have spent an essential part of my time on primary photochemical processes. It would have been difficult to separate physics and chemistry in photoprocesses because both are intimately connected to each other and both together determine what occurs in a system which has absorbed a quantum of light.

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