

DIABATIC AND ADIABATIC PROCESSES IN PHOTOCHEMISTRY

TH. FÖRSTER

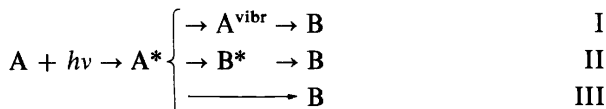
*Institut für Physikalische Chemie der Universität,
7000 Stuttgart 1, Germany, Wiederholdstrasse 15.*

ABSTRACT

Photochemical reactions may be classified as adiabatic or as diabatic whether the chemical change occurs on the same potential energy surface or not. In the adiabatic cases deexcitation occurs either in the reactant (I) or in the product (II) while in the diabatic case it occurs in between them (III). The potential energy surfaces of polyatomic systems are discussed in relation to photochemistry and the possible conditions for the different behaviour of photo-reactions are formulated. Experimental evidence for the appearance of excited products in photoreactions in solution is given.

I. CLASSIFICATION OF PHOTOCHEMICAL REACTIONS

Thermal reactions with rare exceptions occur adiabatically on the lowest potential energy surface. An equivalent statement for photochemical reactions is less easy. They start in one of the electronically excited states of a reactant but end with the products in their ground states. This corresponds to a transition from a higher potential surface of the system to the lowest one. So, in principle, all photoreactions include diabatic processes. If one regards, however, electronic excitation and deexcitation as physical rather than chemical processes one may classify a reaction as adiabatic or as diabatic whether the chemical change takes place on the same potential surface or not. This leads us to a distinction between three different classes of photoreactions in which deexcitation occurs (I) in the reactant(s), or (II) in the product(s), or (III) anywhere in between on the reaction path. Schematically, these classes may be characterized as follows:

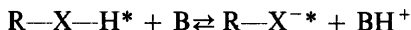


Here A and B represent either single molecules or pairs of them, electronic excitation (either singlet or triplet) is denoted by an asterisk, vibronic excitation by vibr. In our present terminology, class I- and II-reactions are adiabatic while class III-reactions are diabatic.

Class I-photoreactions are hot-ground-state reactions and occur preferentially in the gas phase at lower pressure. They may even be regarded as quasi-thermal reactions because the chemical change occurs exactly as in a (unimolecular) thermal reaction. In a modified form with A^{vibr} a virtual state, the class I-process has, however, been adopted for the theoretical treatment of other photoreactions too¹.

Class II-behaviour is quite common in gas phase photodissociations of diatomic molecules which usually occur under formation of one atom in an excited state. H_2 , I_2 , and alkylhalides are current examples.

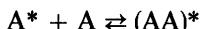
Other class II-reactions occur in solution. There are numerous protolytic photoreactions of the type^{2, 3, 4}



(R: aromatic nucleus; X: $-O-$, $-NH-$, $-COO^-$; B: base, BH^+ : acid).

They result from the alteration of acidity by electronic excitation together with the fast rates of protolytic processes in general. Similar intramolecular protolytic photoprocesses have also been observed⁵.

A further example is the formation and dissociation of excimers⁶



Class II-reactions of any kind proceed adiabatically on the potential surface of the excited state from reactant- to product-configuration. The diabatic process of deexcitation occurs afterwards either by radiation or by radiationless internal conversion.

It is another characteristic feature of class II-photoreactions that they are followed by very fast back reactions. This makes it difficult to observe them at all, and is the reason why they are often not recognized as well-behaved photoreactions. In this respect they differ, however, from other reversible photoreactions only by the rate of the back reaction.

The majority of photochemical reactions in condensed phases belong to class III. Excess vibrational energy is transferred to the surrounding medium so fast that a hot ground state cools down before it has time to react. Moreover, the course of a photochemical reaction depends essentially on the properties of the reacting excited state, such as the bond order distribution for *cis-trans*-isomerizations or the electron density distribution for nucleophilic photosubstitution at the benzene ring⁷ and for the typical dehydration reactions of $n-\pi^*$ -states. Finally, the success of the Woodward-Hoffmann rules in the prediction of photochemical reaction paths⁸ demonstrates convincingly that these reactions start on the potential energy surface of an excited state.

On the other hand, the products of well-behaved photochemical reactions in condensed phases evolve directly in their ground states. With the exceptions summarized under class II, no observations seem to exist on the formation of product molecules in excited singlet- or triplet-states where they might easily have been detected by their luminescence. Obviously, in these reactions, the diabatic process of deactivation occurs neither in the configuration of the reactant(s), nor in that of the product(s), but in a certain intermediate configuration. We may expect, even though the opposite would be difficult to detect, that this deactivation occurs by a radiationless process.

II. POTENTIAL ENERGY SURFACES

The foregoing considerations lead us to a more detailed discussion of potential energy surfaces. In the framework of the Born–Oppenheimer-approximation the potential energy $V_n(Q)$ is the total energy of the system in its n th electronic state with all its nuclei at rest in momentary configuration Q . The corresponding surfaces $V = V_n(Q)$ in V - Q -space are the adiabatic potential energy surfaces of the system.

A chemical or photochemical reaction, as long as it occurs adiabatically, can be described by a reaction path on its potential energy surface. The preferential path of lowest energy leads from the reactant configuration through a valley to a saddle and over this saddle into another valley with the product configuration as its lowest point. Such a preferential path is usually described by a reaction coordinate Q_r which, however, is generally not a normal coordinate of the system. Moreover, it depends on the potential energy surface on which the reaction takes place and should be designated as $Q_r^{(n)}$. This makes it a little dangerous to discuss photochemical reactions by means of two-dimensional potential energy diagrams $V = V_n(Q_r)$.

In the case of a class III-photoreaction an adiabatic transition occurs from the original potential energy surface to that of the ground state at an intermediate configuration. An intersection between both surfaces would make this especially easy. It is, therefore, important whether such intersections exist. In the potential energy diagram along a certain reaction coordinate Q_r , this could give rise to curves like those in *Figure 1*. The non-crossing rule for diatomic molecules makes such intersections extremely unlikely for these and allows them, practically, only for states of different symmetry or, to some extent, of different multiplicity. For polyatomic systems the non-crossing rule is less stringent†. It restricts, however, possible ‘crossings’ to certain singular ‘points’ in Q -space so that they rather are interconnections between the otherwise well separated potential energy surfaces.

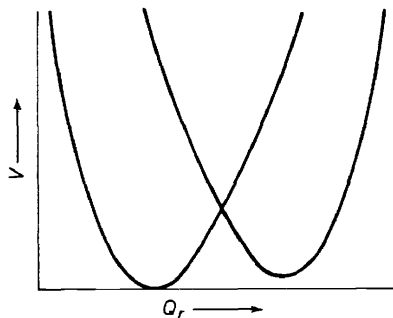


Figure 1. Potential energy diagram for photochemical reaction along a reaction coordinate Q_r .

† E. Teller, *J. Chem. Phys.* **41**, 109 (1937); G. Herzberg and H. C. Longuet-Higgins, *Disc. Faraday Soc.* **37**, 77 (1963). An intersection or interconnection of the potential energy curves or surfaces m and n corresponds to a degeneracy in energy at a certain configuration and requires two different conditions to be satisfied. One of these may be interpreted as the equality in unperturbed energy: $H_{mm} = H_{nn}$, and the other as the absence of a perturbation: $H_{mn} = 0$. With more than one configurational coordinate these conditions can generally be satisfied, even between states of the same symmetry or multiplicity but at singular ‘points’ only.

It is very unlikely that one of these singularities occurs on the preferential reaction coordinate Q_r , or even near to it. One arrives again here at the non-crossing rule, even if in a more relaxed form. In general, the two-dimensional potential energy diagram may well look more like *Figure 2* with 'avoided crossings' instead of actual crossings or interconnections⁹.

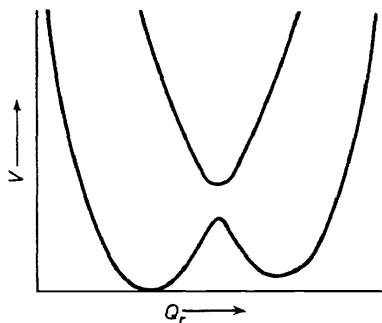


Figure 2. Same as *Figure 1* but with 'avoided crossings'. Pertinent to class III-photoreaction.

Formally, *Figures 1* and *2* represent the potential energy diagrams of an isomerization. Nevertheless, our considerations are valid as well for monomolecular dissociations and for bimolecular reactions of any kind. In principle, even systems with different state-multiplicities might be discussed on the basis of *Figures 1* and *2*. This, however, will not be done here. The only severe oversimplification seems to be the replacement of the different reaction coordinates $Q_r^{(n)}$ by the single coordinate Q_r .

III. ADIABATIC AND DIABATIC REACTION COURSES

Let us now consider the probable conditions for the differences in the courses of photochemical reactions which have led to our distinction between classes I to III. It is true that these differences originate from those in the electronic mechanisms. Nevertheless, a more formal discussion on the basis of potential energy surfaces should be possible. Environmental effects should, of course, also have been taken into account.

The conditions for our class I, the hot ground state photoreaction, are more or less trivial. A sufficiently deep minimum should exist in the potential of the excited state at the reactant configuration in order to provide enough time for internal conversion to the ground state from there. Besides this, the then heavily vibrating molecule should be sufficiently isolated so that it maintains its energy until the reaction occurs.

Some of the conditions for a class II-photoreaction, which occurs adiabatically on the higher potential energy surface, are more or less trivial as well. This surface should have a minimum at the product conformation, lower or at least not essentially higher than that at the reactant configuration if there is one. Furthermore, the energy barrier between both should not be much higher than some kT .

A further condition is less trivial. The potential surfaces between reactant- and product-configuration must be unfavourable for interconversion in this region. To a considerable extent this should be accomplished by the mere existence of an energy barrier in the excited state between both configurations because this would not allow the system to spend much time within that critical region. Besides this, a wide separation in this region between the potential surfaces of both states might be helpful. This implies that the reaction coordinates of both states should not differ too much and that an eventual ground state barrier should not be too high. It is of interest in this connection that all known examples of class II-photoreactions are followed by fast thermal back reactions. The potential energy diagram of *Figure 3* might be representative for class II.

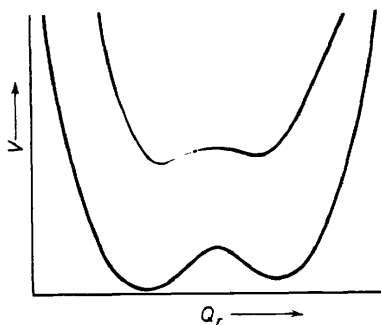


Figure 3. Same as *Figure 2* but pertinent to class II-photoreaction.

In class III the internal conversion occurs between the configurations of reactant and product. This implies that such a configuration is easily obtainable on the excited state surface from the reactant side. Besides this, internal conversion should readily occur from there. A sufficiently deep minimum at this configuration would be favourable for this. A small separation between both surfaces, and also some difference in slope and in curvature in that region would be helpful too, as well as a difference in the reaction coordinates Q_r . These conditions are essentially those which result from an avoided crossing such as represented in *Figure 2*.

It might seem from these considerations that the existence of a barrier or of a hole in the potential energy surface of the excited state near the critical configuration would decide between class II- and class III-behaviour and so between the diabatic or adiabatic course of a photoreaction. This is, however, very probably an over-simplification since the other features of the potentials mentioned in our preceding discussion might play more than a contributing role. Besides this, the effective mass belonging to the reaction coordinate should also be of importance as in other cases of internal conversions.

Furthermore, we should expect that the distinction between our classes II and III might be not an absolute one but that intermediate cases would exist. For a reaction with predominant class II-character a low barrier in the excited-state potential, together with other features as discussed before,

might result in the deactivation of a certain fraction of the reacting system before reaching the product state. The opposite might occur with a class III-reaction in the case of a shallow minimum from which the system might escape to the product configuration before it becomes deactivated.

IV. A SEARCH FOR INTERMEDIATE CASES

Guided by such considerations Dr Menter and I have tried to find out whether in a well-behaved photochemical condensed phase reaction at least a small fraction of electronically excited product molecules can be identified. It seemed to us that the photochemical dissociation of dianthracene¹⁰ might be suitable for this. A semiquantitative potential energy diagram of this reaction, based on available data, is represented in *Figure 4*. There is evidence that this reaction as well as the opposing photodimerization occurs from the lowest excited singlet state. It is exothermic in ground- and excited-state so that energetically the formation of singlet-excited anthracene molecules should be possible. One would then expect anthracene fluorescence under excitation of dianthracene which has its first absorption maximum at 270 nm.

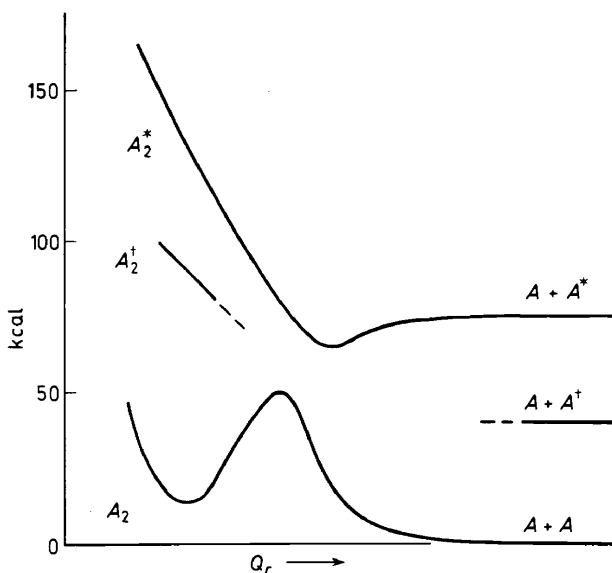


Figure 4. Tentative potential energy diagram for formation and dissociation of anthracene dimer. Asterisk : excited singlet, dagger : triplet.

We did not expect any drastic effect since this would not have escaped previous observations. However, even with a very sensitive technique, which would have been able to detect fluorescence with a quantum yield smaller than that of anthracene by a factor of 10^4 , we found nothing. Obviously, less than such a small fraction of the originally excited molecules escapes deactivation along the reaction path.

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A little disappointed by this negative result we then tried the same with 9-methylanthracene. This compound behaves similarly to anthracene with the exception that in concentrated solution it forms a fluorescing excimer^{11, 12} which anthracene does not. In *Figure 4*, the minimum in the potential energy curve of the excited state is intended to represent this excimer state from which, however, fluorescence is not observable with anthracene itself.

We next looked for fluorescence in the excimer region under excitation of di-9-methylanthracene. Here, where our detection limit is still less than in the monomer region, we found a fluorescence with a quantum yield of about 2×10^{-4} . Obviously, a fraction of excited dimer molecules, of a similar magnitude, succeeds in attaining the excimer configuration before deactivation occurs. The fraction is very low indeed. This shows, if the excimer configuration can be supposed to be somewhere in between that of dimer and monomer^{13, 14, 15}, that radiationless deactivation on the dimer side is very efficient.*

Although this result is in no way spectacular, similar investigations might be useful in order to give some information on potential energy surfaces of photochemical systems and also on the until now very badly understood deactivation processes occurring between them.

ACKNOWLEDGEMENTS

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* Note added in proof: In recent experiments monomer fluorescence, also resulting from dimer absorption, has been detected here too.