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Reactivity of Organic Compounds in an Excited Electronic State

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The review deals with the reactivities of complex organic compounds in an excited state; the characteristics of the electronic structure of the molecules, which play a fundamental rule in photochemical reactions, are discussed.
The bibliography includes 79 references.

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I. INTRODUCTION

On absorption of a light quantum, the molecule passes to an excited singlet state (a direct transition to a triplet level is usually forbidden). The energy of this state is determined both by the magnitude of the absorbed quantum and by the position of the energy levels in the molecule. In the condensed phase, a series of relaxation processes takes place very rapidly (over a period $\leq 10^{-12}$–10^{-13} s). Among these, the most important is spontaneous transition from the highest to the lowest excited levels and the establishment of the equilibrium configuration of the nuclei for the given state (the excess vibrational energy is then transmitted to the medium).

At the lowest excited level, the molecule can persist for a longer period (10^{-9}–10^{-7} s at the singlet level and 10^{-6}–10^{-1} s at the triplet level). The transition to the ground state now involves both the possibility of non-radiative deactivation of the molecule and the emission of excess energy as luminescence.

Photochemical reactions can in general occur at any instant after the absorption of light by the molecule and therefore can compete with both rapid and slow deactivation processes.

As an example, we shall consider the homolytic photochemical decomposition of a molecule. On absorption of light, the molecule can easily pass to an antibonding excited level and its dissociation takes place over a period of about 10^{-12}–10^{-13} s. If there is sufficient time for the molecule to pass to a lower level, which may prove stable, its decomposition can be caused either by the fact that its vibrational energy exceeds the dissociation energy of any one bond or by pre-dissociation. Dissociation processes are also possible during the return to the ground level. In the latter case the molecule in the ground state has a much higher vibrational energy than the thermal energy of the molecules in the surrounding medium. For such a "hot" molecule to undergo a chemical transformation, the process must be very rapid, since the excess vibrational energy is dissipated over a period of about 10^{-12} s.

Naturally this approximate scheme does not exhaust all possible situations, since triplets states, $n\pi^*$ states, and charge-transfer states may play a major role in the chemical reactions of the excited molecule. Moreover, different levels can exert a mutual influence on one another, becoming mixed, which also precludes a rigorous classification.

Fortunately, in many photochemical reactions (this applies also to the majority of the reactions considered in the review) the molecules involved in them pass to the lowest excited levels which have minima on their potential surfaces, greatly facilitating the consideration of the process mechanism. We can assume that, owing to their fairly long lifetime, such excited molecules are in a thermal quasiequilibrium with the surrounding medium and the mode and rates of their reactions are determined by the energy barrier on the reaction pathway. This approach is potentially similar to that employed in the discussion of reactivities of molecules in the ground state. Therefore, in order to estimate the reactivities of excited molecules, one should consider the same parameters—the rate constant and the activation energy—as for dark processes. However, in photochemical reactions this is not a simple task, since usually it is possible to measure only the quantum yields of the processes. For a unimolecular reaction, the quantum yield $\varphi = k\tau$ and for a bimolecular process $\varphi = k\tau c$, where k is the reaction rate constant, τ the lifetime of the excited molecules of the absorbing species, and c the concentration of the second component. However, τ can be by no means always determined.

The second factor which hinders the study of the reactivities of various excited molecules is the absence of activation energy in many photochemical reactions. In particular, this casts doubt on the possibility of employing the transition state theory for the interpretation of the results, since the fundamental postulate of the theory concerning the equilibrium between the activated complex and the initial molecules breaks down. It may be that the excited molecule in such reactions should be regarded as the species which has already risen above the reaction "hump". Then the rate of the process will be determined solely by the probability factors which enter into the pre-exponential factor.

It must be emphasised that the reactivity of an excited molecule is not caused solely by the fact that it has greater energy available than the surrounding molecules. The electronic structure of the excited molecule differs from its structure in the ground state. Therefore the equilibrium positions of the nuclei must be different. We are dealing essentially with a new molecule having new properties. In other words, the excited molecule can react in a completely different manner than the molecule in the ground state.

In the present review an attempt has been made to describe the current approaches to the study of the reactivity of excited organic molecules. For this purpose, we have chosen classes of photochemical reactions which

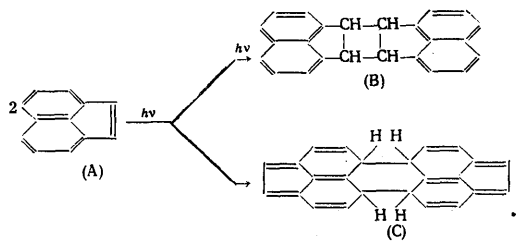
have been most thoroughly investigated in this respect. There are good reviews of many of these reactions and some are described in monographs[1-10]. Nevertheless it is desirable to consider these data in one review from a single standpoint.

II. PHOTOCHEMICAL FORMATION AND OPENING OF RINGS

1. Elementary Treatment

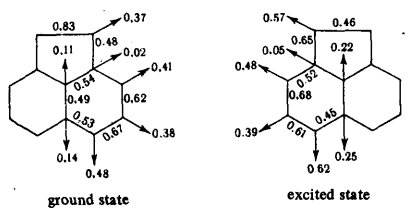
When an attempt is made to explain why the action of light on a molecule causes preferential dissociation or formation of a particular bond, the first idea that comes to mind is to examine how the reactivity indices change when the molecule passes to an excited state. The success of this simple approach may be illustrated using as an example the photocyclisation reactions of certain aromatic hydrocarbons.

This was first done by Crawford and Coulson[11] in a study of the photodimerisation of acenaphthylene[12], which might proceed in two different ways:



(I)

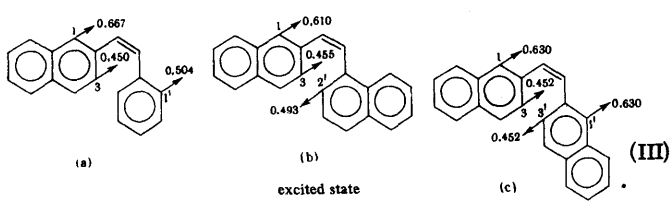
In fact the photochemical reaction leads to the formation of compound (B) only. In order to account for this finding, Crawford and Coulson compared the free valence indices and the bond orders of the molecule (A) in the ground and first excited states calculated by the simple Hückel molecular orbital method:



(II)

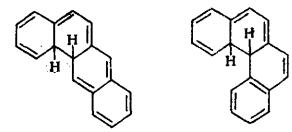
Scheme (II) shows that, on excitation of the molecule (A), the greatest decrease of bond order and increase of the free valence index of the atoms occurs in the ethylenic bond. This in fact leads to preferential dimerisation at this bond. The absence of the dimer of type (C) can probably be accounted for by the fact that this involves the formation of the energetically less favourable quinonoid structure, although the free valence indices in the para-α-positions of the naphthalene ring of substance (A) increase appreciably in the excited state.

The photocyclisation reactions of a number of naphthyl-substituted ethylenes have been interpreted similarly[13]:



(III)

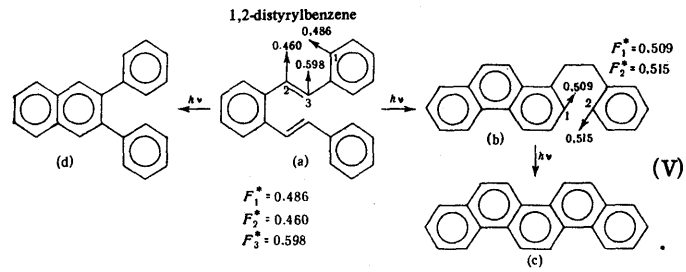
The cyclisation reaction can take place at both the α- and β-positions of the naphthalene ring. For example, with compound (a) one must consider the possibility of forming the following two isomers:



(IV)

The free valence indices for the excited molecules shown in scheme (III) suggest that the cyclisation should involve the formation of a 1,1'-bond (the sum of the F_1^* and F_8^* indices is a maximum). Indeed, experiment showed that cyclisation takes place only at the α-positions, although this mode of reaction is sterically more hindered.

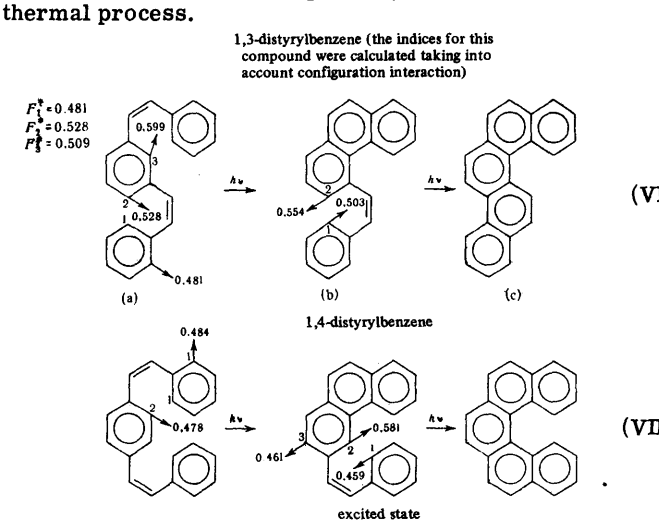
The photocyclisation reactions of distyrylbenzenes (V)–(VII) have been interpreted similarly[14]:



(V)

As in the preceding case, the cyclisation of distyrylbenzene should involve ring closure at the sites of the maximum values of $F_8^* + F_1^*$. For 1,3- and 1,4-distyrylbenzenes or their cyclisation products, this rule indeed holds. However, the reaction of 1,2-distyrylbenzene follows the (a) → (b) → (c) pathway instead of (a) → (d), probably owing to the steric hindrance in the formation of (d).

The ambiguity of the treatment of alternant hydrocarbons based on a comparison of the reactivity indices in the excited state arises because the positions in the molecule which are the most reactive in the excited state (for example have the highest free valence) are also the most reactive in the ground state. Therefore, in the absence of additional data, it is difficult to rule out the possibility that the reaction involves vibrationally excited molecules in the ground electronic level, which are formed when the electronic excitation energy is degraded. The reaction of such "hot" molecules is probably similar to the thermal process.



(VI)

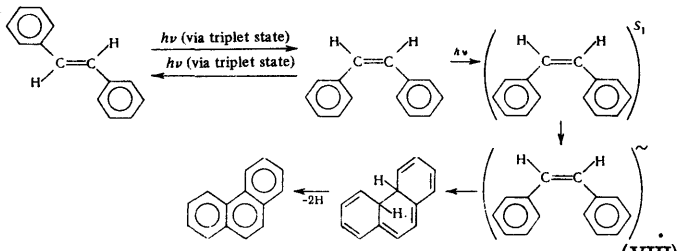
(VII)

According to Gusten and Klasing[15], the cyclisation of stilbene to 4a,4b-dihydrophenanthrene takes place in the same way (in the presence of oxidants, oxygen, air, iodine, etc., the reaction proceeds as far as the formation of phenanthrene). In a study of the photochemical cyclisation of various *m*- and *p*-substituted stilbenes, Gusten and Klasing found that for *m*-substituted stilbenes there is a satisfactory linear correlation between the sum of electron densities in the ground state at the *o*-carbon atoms involved in the new bond and the quantum yield of the reaction. For the excited electronic state of *m*-substituted stilbenes and also for the ground and excited states of *p*-substituted stilbenes, there is no correlation whatever between the electron densities and the quantum yield of the cyclisation reaction. Gusten and Klasing[15] explain this finding by postulating that the cyclisation takes place in a vibrational excited state of the molecule for stilbene and its derivatives. The absence of an effect by *p*-substituents on the rate of reaction was explained by the fact that these substituents are in the *m*-position relative to the reacting carbon atoms and therefore have little influence on the electron densities at these atoms.

On the other hand, *p*-substituents cause a significant shift of the absorption band maximum of stilbene towards longer wavelengths. There is a linear relation between the frequency of the absorption maximum and the quantum yield of the cyclisation reactions of the *p*-substituted derivatives. The authors believe that the higher the energy of the excited electronic level from which the molecule passes to the ground level, the greater its store of vibrational energy and the faster its cyclisation reaction.

A number of facts[16] indicate that the photochemical cyclisation of stilbene involves a stage in which *cis*-stilbene molecules in a singlet excited electronic state are formed. For example, on excitation to the triplet level via a triplet–triplet energy transfer, cyclisation does not occur[17,18]. Possibly the vibrational energy of the "hot" molecule formed on transfer from the triplet state is insufficient for effective cyclisation.

Thus the following scheme may be formulated for the photochemical reaction for stilbene and its derivatives.

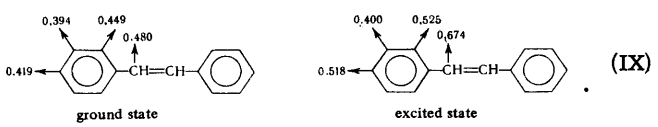


(VIII)

The symbol ~ denotes vibrational excitation.

The fact that, on pyrolysis of *cis*-stilbene, the product is also phenanthrene in a high yield[19] may be regarded as definite confirmation of the involvement of vibrationally excited stilbene molecules in the cyclisation reaction.

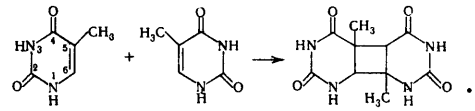
It is interesting to note that, regardless of whether electronically excited or vibrationally excited stilbene molecules are involved in the reaction, the dimerisation process which yields tetraphenylcyclobutane should compete with cyclisation to phenanthrene. The free valence indices in the ground and excited states show that the first reaction should be faster:



(IX)

Indeed, the dimerisation reaction predominates in concentrated solutions.

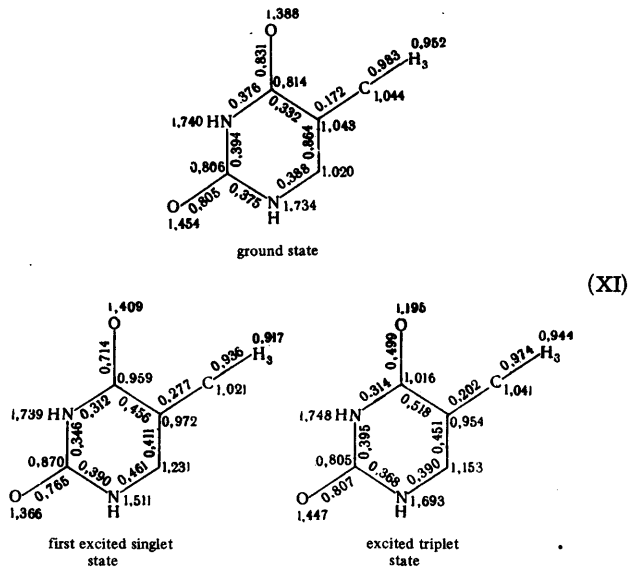
Using these simple concepts, Pullman and coworkers[20] examined the reactivities of pyrimidine rings in their photochemical dimerisation. This reaction probably plays an important role in the photochemistry of nucleic acids and in particular of DNA (nucleic acids contain pyrimidine rings as structural units). Pyrimidines are dimerised via the interaction of 5-C and 6-C atoms of two pyrimidine rings with formation of a cyclobutane ring. For example, thymine cyclises according to the mechanism:



(X)

Comparison of the electron densities and bond orders in the ground and excited states of thymine (XI) makes it clear why cyclisation takes place at the carbon atoms in the 5- and 6-positions of the thymine ring[21]†:

electron densities and bond orders of thymine



(XI)

It is noteworthy that the difference between the reactivity indices of the triplet and singlet excited states is insufficient to yield a definite conclusion about the multiplicity of the molecules involved in the reaction.

Thus simple comparison of the reactivity indices makes it possible in certain cases to obtain a definite idea about the process mechanism. However, in many instances the result is ambiguous.

A more general approach, based on the rules of conservation of orbital symmetry formulated by Woodward and Hoffmann, is possible for the interpretation of the cyclisation and cyclodecomposition reactions of symmetrical molecules.

†The calculation was carried out by the self-consistent field method taking into account the interaction of singly excited states.

2. Reactions with Conservation of Orbital Symmetry

It was mentioned above that one of the important problems frequently encountered in the study of reactivities in photochemical reactions is whether electronically excited molecules or hot molecules in the ground electronic level are involved in such reactions. We have seen that usually an answer to this question cannot be simply obtained. However, there are many reactions, the so called concerted reactions, for which it is possible to predict, on the basis of considerations related to orbital symmetry, whether the reaction proceeds via an excited electronic state or a ground electronic level. These considerations were first put forward by Woodward and Hoffmann [22,23] and then in a more rigorous form by Longuet-Higgins and Abrahamson [24]. They are based on the symmetry of the molecular orbitals of the starting materials and reaction products and reduce to the requirement that the symmetry be retained in the course of the reaction. This can be made clear by examples discussed in the literature [22-24]—the cyclodimerisation of ethylene to cyclobutane and the cyclisation of butadiene to cyclobutene.

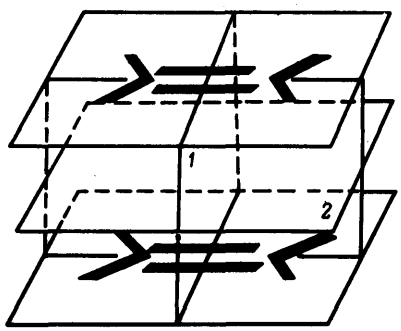


Figure 1. Mutual approach of two parallel ethylene molecules [3].

In order to form two σ bonds of cyclobutane from two π bonds of ethylene in its cyclodimerisation, it is necessary that the ethylene molecules should approach one another until the $p\pi$ electron clouds of the carbon atoms overlap. We imagine that during such approach the molecules are arranged parallel to one another and consider the symmetry of the system as a whole relative to the two planes *1* and *2* (Fig. 1).

If the ethylene molecules are in the ground state (the π bonding molecular orbital), two cases are possible: either the molecules approach one another so that components of the π-electron clouds of the same sign overlap or the approach is such that components of the π-electron clouds of opposite sign overlap (Fig. 2).

In the first case a bonding interaction takes place between the ethylene molecules—a combination of two π-electron functions of ethylene symmetrical relative to both planes *1* and *2* (such combination will be referred to as *SS*). In the second case a weak repulsion arises between the approaching molecules and the electronic combination is symmetrical relative to plane *1* and antisymmetric relative to plane *2* (*SA*). If the π-electron function of one ethylene molecule is denoted by π_1 and that of the other by π_2, the first combination may be characterised by the function $\pi_1 + \pi_2$ and the second by $\pi_1 - \pi_2$.

If we now consider what happens when two ethylene molecules in an excited electronic state (π_1^* and π_2^*) approach one another, examination of Fig. 2 readily shows that again there is a possibility of a bonding combination $\pi_1^* + \pi_2^*$ characterised by *AS* symmetry and an antibonding combination $\pi_1^* - \pi_2^*$ with *AA* symmetry.

The symmetry of the different states of cyclobutane can be treated similarly. The difference is that the carbon atoms in the cyclobutane molecule are linked by σ bonds. Here the bonding states are evidently $\sigma_1 + \sigma_2$ and $\sigma_1 - \sigma_2$ with *SS* and *AS* symmetries. The antibonding states are $\sigma_1^* + \sigma_2^*$ and $\sigma_1^* - \sigma_2^*$ with *AS* and *AA* symmetries.

We now draw lines connecting the states of cyclobutane and of the system of two ethylene molecules with the same symmetry, as in Fig. 2, and obtain a correlation diagram similar to those proposed at one time by Hund and Mulliken [25] to elucidate the relations between the molecular

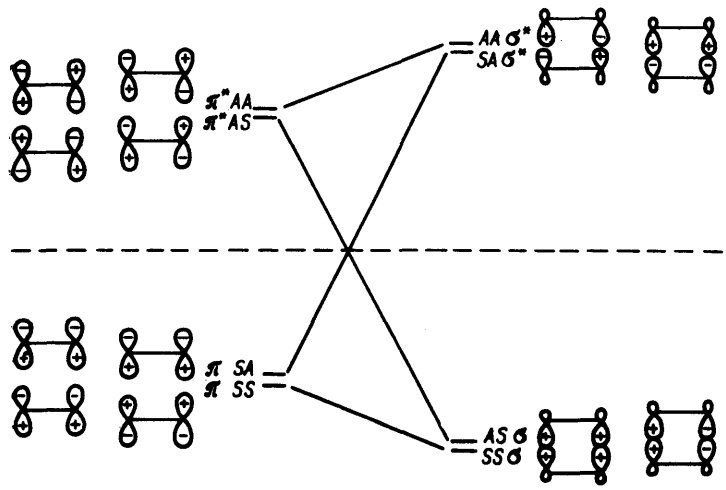


Figure 2. Correlation diagram for the formation of cyclobutane from two ethylene molecules [8].

orbitals of diatomic molecules and the atomic orbitals of their constituent atoms.

By considering the two approaching ethylene molecules as a single formation, we distribute four π electrons among its electronic orbitals in accordance with the Pauli principle. Evidently the lowest state of this system is the symmetrical (S) state $(SS)^2(SA)^2$. Similarly the lowest electronic state of isobutane should be $(SS)^2(AS)^2$ with S symmetry in which four σ electrons are located. The lowest level of a combination of two ethylene molecules should be correlated with the doubly excited cyclobutane state $(SS)^2(SA)^2$ and the lowest level of cyclobutane should be correlated with the doubly excited state $(SS)^2(AS)^2$ of the system of two ethylene molecules. However, since these states have the same symmetry, the non-crossing rule, according to which levels of the same symmetry do not intersect owing to electron repulsion, applies to them.

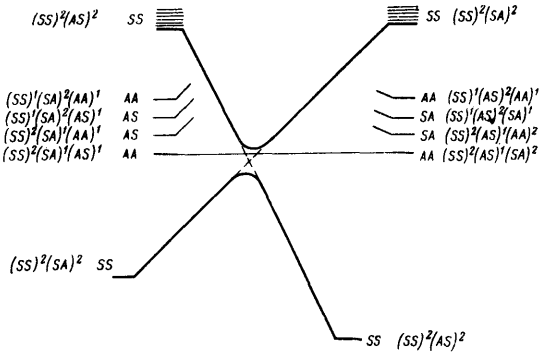


Figure 3. Diagram of electronic states for the formation of cyclobutane from two ethylene molecules. The symmetry of the states is defined by the relations[8]

$$S \times S \to S \leftarrow A \times A,$$
$$S \times A \to A \leftarrow A \times S.$$

As a result the diagram assumes the form shown in Fig. 3, where the ground level of the two ethylene molecules is seen to be correlated with the ground level of cyclobutane. The highest excited levels are also correlated with one another. It is evident from the diagram that, for the conversion of the two approaching ethylene molecules in the ground state into cyclobutane with retention of symmetry, the system must overcome an energy barrier. Therefore such a process is unlikely. In a situation where two π electrons of the ethylene molecules are promoted to excited orbitals—the state in which the conversion into cyclobutane can occur without an activation energy—is also improbable. However, the transition of one π electron of ethylene to a lower excited state yields the symmetrical function $(SS)^2(SA)^1(AS)^1$, which is correlated with the lowest excited state $(SS)^2(AS)^1(SA)^1$ of the cyclobutane molecule, corresponding to the excitation of one π electron. In other words such a transformation is allowed by symmetry and does not require an activation energy, as can be seen from the diagram. At the same time this state can be readily achieved when ethylene is subjected to the action of light [for many compounds, such an excited dimer (excimer) can be actually detected spectroscopically]. From this it follows that the dimerisation of ethylene should have a photochemical and not a thermal mechanism‡.

The correlation diagrams also make it possible to discover the relations governing the reversible cyclobutane ⇌ butadiene reaction. Such reactions, which involve the formation of a σ bond from two π electrons without a change in the number of carbon atoms in the molecule, are called electrocyclic. Cyclobutene can be converted into butadiene via two pathways (Fig. 4): the dissociation of the σ bond between the C_1 and C_4 atoms in such a way that the methylene groups $H_3 \diagdown C_1 \diagup H_1$ and $H_4 \diagup C_4 \diagdown H_2$ rotate either in the same direction (Fig. 4*a*) or in the opposite directions (Fig. 4*b*). The first pathway is called conrotatory and the second disrotatory. Evidently, in conrotatory ring opening, the system retains a two-fold symmetry axis in the course of the entire reaction. In disrotatory ring opening, the system retains a plane of symmetry. This is also true of the converse reaction—the cyclisation of butadiene.

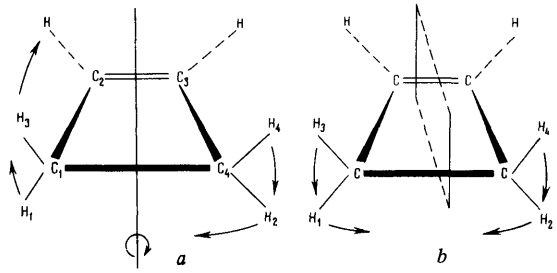


Figure 4. Symmetry of the conrotatory (*a*) and disrotatory (*b*) transformations[26].

Naturally if the polyene or the cyclic form do not contain substituents, the conrotatory and disrotatory transformations cannot be distinguished experimentally. However, if one hydrogen atom at each of the extreme carbon atoms is replaced by a substituent (as has been done in Figs. 5*a* and 5*b*), each type of rotation gives rise to different stereoisomers.

Using the same principle of the conservation of orbital symmetry, it is possible to construct correlation diagrams for these reactions[8], as was done for ethylene. The diagrams show that the conrotatory cyclobutene ⇌ ⇌ butadiene interconversion should have a thermal mechanism and the disrotatory interconversion should take place as a photochemical process involving the first excited states.

The same conclusions were reached in the first study by Woodward and Hoffmann[22] with the aid of simpler considerations based on the hypothesis that the nature of the electrocyclic reaction is determined by the symmetry of the highest occupied orbital of the acyclic product. For the ground state of butadiene, the ψ_2 orbital is of this kind

‡In this case thermal processes are understood as processes in which vibrationally excited molecules, formed on transition of the molecule from an excited electronic to the ground state, are involved.

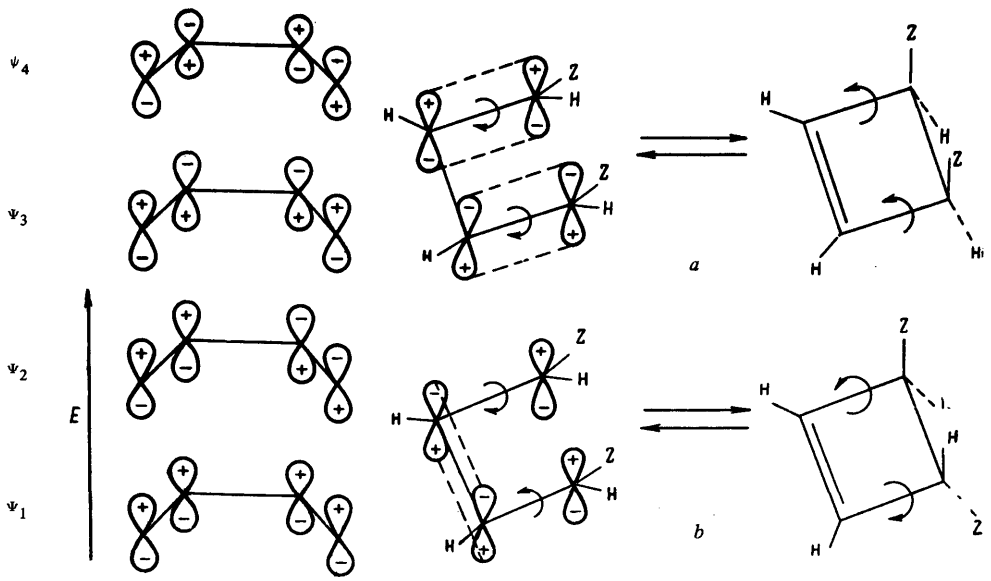
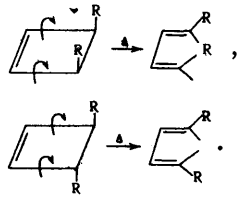


Figure 5. Schematic illustration of the butadiene ⇌ cyclobutane electrocyclic reaction[26].

(Fig. 5). Fig. 5*a* shows that the conversion of the π bond into a bonding σ linkage in the ring as well as the reverse process require a conrotatory transformation. For the photochemical reaction, where the highest occupied butadiene level is ψ_3 (Fig. 5*b*), cyclisation and ring opening are disrotatory processes. Although these considerations do in fact give rise to certain doubts[24], nevertheless they constitute a simple and convenient procedure and lead to the same conclusions as the correlation diagrams. For example, examination of the highest occupied orbitals leads to the prediction that, for the cyclopropyl cation ⇌ ⇌ allyl cation electrocyclic reaction, the thermal process should be disrotatory and the photochemical process conrotatory[22]. This is also indicated by the correlation diagram[24]. The hexatriene ⇌ cyclohexadiene reaction should also have a thermal mechanism for the disrotatory transformation and a photochemical mechanism for the conrotatory transformation.

Generalising all these results, Woodward and Hoffmann concluded that, for all systems the acyclic components of which contain $4n$ π electrons (n = 0, 1, 2, 3, ...), electrocyclic reactions involve a conrotatory thermal mechanism and a photochemical disrotatory mechanism. For a system with an acyclic component containing $4n + 2$ π electrons, the thermal and photochemical reactions take place with rotations in the opposite sense. This relation in fact constitutes one of the familiar Woodward–Hoffmann rules.

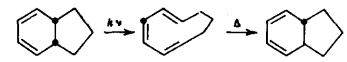
According to the Woodward–Hoffman rules, the thermal opening of the cyclobutene ring with substituents in the 1- and 4-positions leads to the formation of isomers corresponding to the conrotatory process[27-29]:



(XII)

The symbol Δ denotes heating and R = CH_3, $COOCH_3$, CH_2OTs, or Cl.

The sequence of the transformations of the *cis-cis-cis*-cyclonona-1,3,5-triene is very instructive[30,31]:



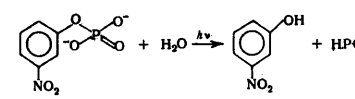
(XIII)

The principle of the retention of orbital symmetry is obeyed by all concerted organic reactions[8]. These include the Diels–Alder reaction, certain rearrangements (the Claisen, Cope, and sigmatropic rearrangements), etc. "Selection rules" have also been formulated for these reactions.

III. PHOTOCHEMICAL SUBSTITUTION REACTIONS OF AROMATIC COMPOUNDS

The scope and disadvantages of the simple molecular orbital method for the interpretation of the chemical behaviour of excited molecules can also be discovered by considering photochemical heterolytic substitution reactions involving aromatic substances.

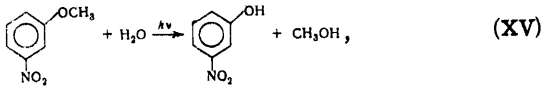
In 1956 Havinga et al.[32] observed that, when aqueous solutions of nitrophenyl phosphate and sulphate esters are illuminated, they are hydrolysed to nitrophenol and the corresponding acid. For example:



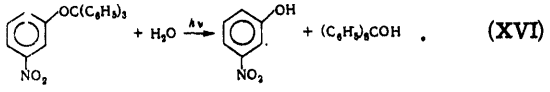
(XIV)

At the same time, in the absence of light, these substances are quite stable to water. It is particularly surprising that the photochemical hydrolysis takes place with the maximum quantum yield when the ester group is in the *meta*-position relative to the nitro-group, while the *ortho*- and *para*-derivatives are relatively inactive under the action of light. In the usual dark nucleophilic substitution reactions, the nitro-group should be *ortho*- and

para-directing regardless of whether the reaction of the substituting agent is with a fluorine (sulphur) atom or a ring carbon atom. Experiments with *m*-nitrophenyl phosphate in $H_2{}^{18}O$ showed that at pH ≤ 12 the photochemical hydrolysis involves the reaction of water with the phosphorus atom, while at pH > 12 the reaction is with a ring carbon atom[33]. Nucleophilic substitution takes place also with CH_3NH_2, CH_3OH, etc. the products being *m*-$NO_2C_6H_4NHCH_3$, *m*-$NO_2C_6H_4OCH_3$, etc. Photochemical hydrolysis has likewise been observed with *m*-nitroanisole[32,34], *m*-nitrophenyl trityl ether, and *m*-cyanophenyl trityl ether[35].



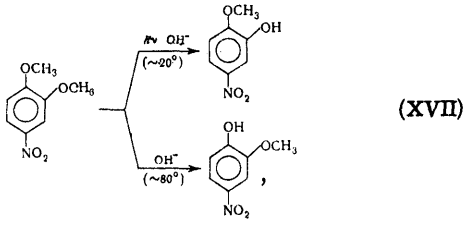
(XV)



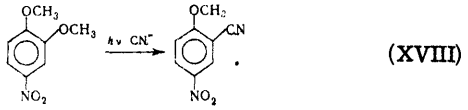
(XVI)

The second reaction does not take place in the dark, although the corresponding *p*-isomer readily hydrolyses at 25°C.

The selectivity of the photochemical reaction is shown particularly clearly when identical substituents are present in the ring in both *m*- and *p*-positions (4-nitroveratrol)[36,37]:



(XVII)

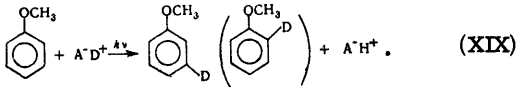


(XVIII)

The reaction of 4-nitroveratrol with methylamine takes place similarly[38].

Photochemical electrophilic substitution reactions include deuterium exchange in aromatic compounds, which was observed independently by de Bie and Havinga[39] and by Kuz'min, Berezin, and coworkers[40].

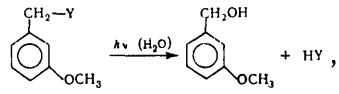
De Bie and Havinga[39] studied light-induced deuterium exchange between anisole and deuteroacetic and trifluorodeuteroacetic acid. It was found that the photochemical substitution of hydrogen in the benzene ring by deuterium takes place only in the *ortho*- and *meta*-positions, the *para*-position is almost inactive:



(XIX)

Kuz'min et al.[40] studied the photochemical exchange of deuterated naphthalene and anthracene with sulphuric acid. The rate of exchange was found to depend on the acidity of the medium, which is characteristic also of dark heterolytic substitution reactions.

Zimmerman and Sandel[41] compared the photochemical hydrolytic reactions of *m*- and *p*-methoxybenzyl acetates, 3,5-dimethoxybenzyl acetate, and *m*-methoxybenzyl chloride in aqueous dioxan solutions. In all cases when the substituted benzyl group was in the *meta*-position, photochemical hydrolysis occurred in a high yield (the presence of two methoxy-groups in the *meta*-position greatly increased the role of hydrolysis compared with homolytic radical decomposition):



(XX)

where Y = OAc or Cl. *Para*-derivatives are scarcely hydrolysed. In this case substitution takes place in the side chain although it is evident that the electron-donating substituent activates the *meta*-position with respect to the photochemical reaction, as in ring substitution.

The results have been interpreted[34,39-43], by comparing the electron densities at different atoms in the molecule. On transition of the molecule from the ground to an excited electronic state, the electron densities change, which may be illustrated for the benzyl cation and anion as examples[41]. Here the $-CH_2^+$ and $-CH_2^-$ groups play the role of electron-accepting and electron-donating substituents (Fig. 6).

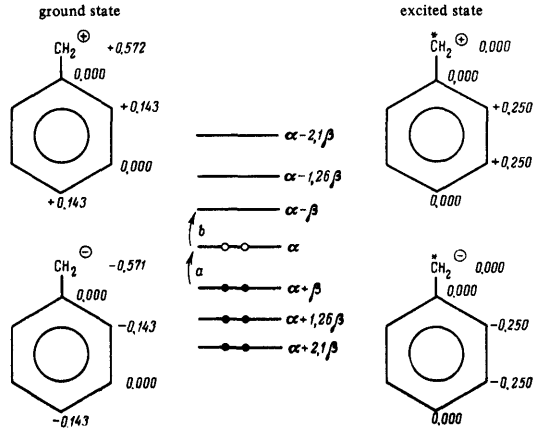
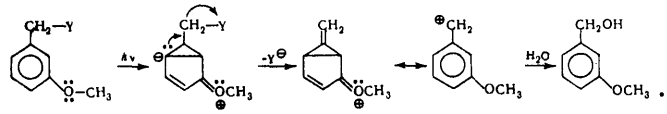


Figure 6. Charge distribution in the benzyl cation and anion[41].

Fig. 6 shows that in the ground state positive and negative charges in the cation and anion are localised in the *ortho*- and *para*-positions, while in the first excited state the charges are localised in the *ortho*- and *meta*-positions. This simple example shows that excitation of the molecule should promote both nucleophilic and electrophilic substitution in the *ortho*- and *meta*-positions. In order to account for reaction (XX) Zimmerman and Sandel[41] suggested that in the excited state of methoxybenzyl derivatives the negative charge is localised at the Y substituent with subsequent dissociation of the molecule to give the methoxybenzyl cation:



(XXI)

Similar charge distributions were obtained also by a more rigorous examination of substituted benzenes using the "molecule in molecule" method[41,43].

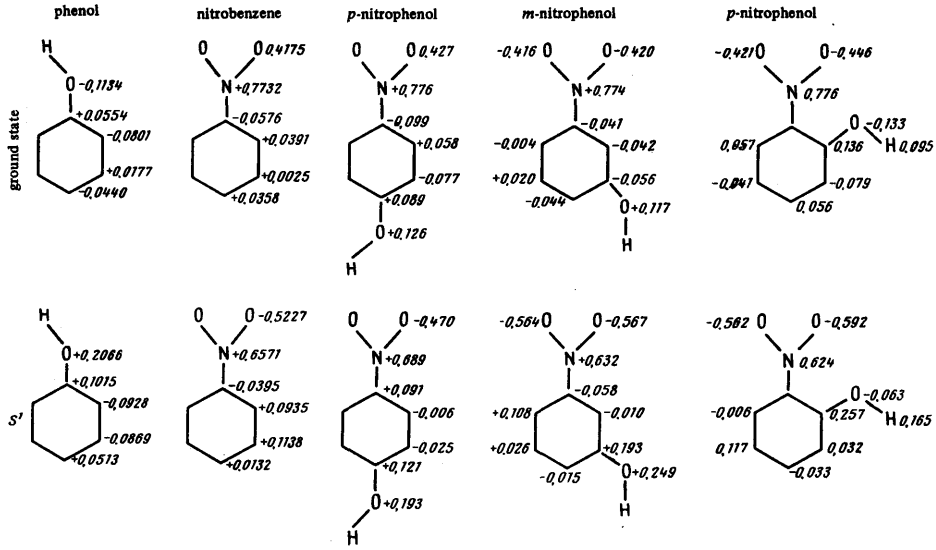


Figure 7. Charge distribution in the ground and lowest excited singlet ($\pi-\pi^*$) states of substituted benzenes[34].

Qualitatively the same redistribution of electron density on excitation of the molecule was obtained by de Bie and Havinga[39] by a calculation using the self-consistent field method for specific phenol (anisole analogue), nitrobenzene, and nitrophenol molecules (Fig. 7).

Thus the localisation of a negative or positive charge at a particular site in the excited molecule probably determines the most favourable site of attack by electrophilic or nucleophilic substituents. A number of data[34,36] clearly show that singlet molecules in the first $\pi-\pi^*$ excited state are involved in the reaction.

The above approach to the estimation of the reactivities of excited molecules in substitution reactions is quite analogous to the approaches employed for the estimation of the reactivities of molecules in the ground state in which a π complex is adopted as a model of the transition state. In this case electron density is a characteristic parameter determining the activation energy for the process. However, according to some data[34,36], the activation energy for photochemical substitution reactions is close to zero. Consequently the employment of reactivity indices such as electron density within the framework of the activated complex concept gives rise to certain doubts[44,45], as already stated. Certain qualitative considerations[34,44] reduce basically to the fact that Coulombic interaction forces arise between atoms at which positive or negative charges are located and between the substituting agents, increasing the reaction cross-section at these particular sites in the molecule. Such concepts are largely intuitive and are not related to a specific reaction model.

One can put forward also another explanation, assuming that the lower experimental activation energies for photochemical reactions are only apparent. Indeed if the substituting agent behaves as a quenching agent, it is quite likely that the quenching process follows the same pathway as the photochemical reaction[34,46]. Then both competing processes (quenching and chemical reaction) should have similar activation energies and an increase of temperature should increase the rates of both processes and should not alter their relative contributions and hence the quantum yield of the reaction. Fig. 8 illustrates a possible mechanism for the substitution reaction.

A clear representation of the intersection in space of the potential surfaces for the reactions was proposed by Kuz'min[47,48]. Like Havinga, he believes that the reaction proceeds non-adiabatically, i.e. in the course of the reaction the electronic excitation energy is degraded. In agreement with the spirit of Nagakura's idea[50], Kuz'min[47-49] believes that in the excited state too the heterolytic substitution reaction is preceded by electron transfer.

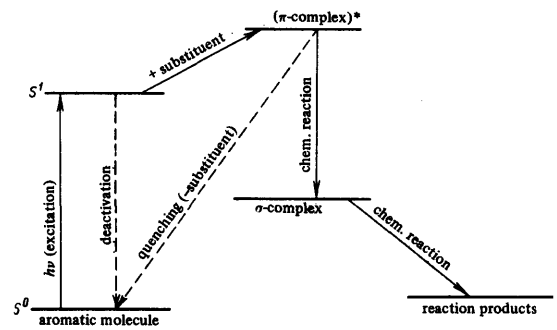
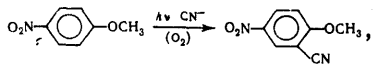


Figure 8. Schematic illustration of the elementary processes in photochemical substitution in the aromatic ring[34].

It is noteworthy that not all photochemical heterocyclic substitution reactions proceed in accordance with the distribution of electron density in the excited molecule. For example, photochemical deuteration of nitrobenzene takes place only in the *para*- and *meta*-positions[39] although the difference between the electron densities in the *meta*- and *ortho*-positions is insignificant (Fig. 7).

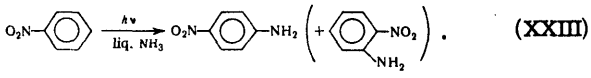
Photochemical cyanation of *p*-nitroanisole takes place in the *o*-position relative to the alkoxy-group [51]:



(XXII)

although according to Fig. 7 this position should be least favourable for nucleophilic substitution.

The position where nitrobenzene is aminated in liquid ammonia [52] is also inconsistent with charges on the ring:



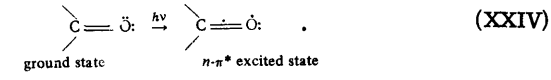
(XXIII)

Havinga and coworkers [36] explain the path of this reaction using the fact that it involves neutral ammonia molecules, and that the electron density near different carbon atoms in the ring should therefore be no longer of decisive importance. In this case a σ complex may be adopted t as a model of the transition state and the localisation energy is best employed as a reactivity index. It is also possible that reaction (XXIII) involves hot molecules (after the conversion of the molecule to the ground state). Then preferential formation of the *para*-substituted derivative is consistent with the distribution of electron density in the molecule.

IV. ABSTRACTION OF HYDROGEN BY KETONES

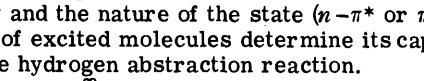
A fairly striking effect of the structure of molecules on their reactivity in the excited state is revealed by a qualitative examination of photochemical reactions of ketones. These constitute one of the most important and one of the most thoroughly investigated branches of organic photochemistry. They are considered in almost all monographs on photochemistry and in many reviews (see, for example, Refs. 1–5, 7, 53). Here we shall confine ourselves to a discussion of the relevant aspects of certain reactions involving the abstraction of hydrogen by the carbonyl group.

The specific features of the photochemical behaviour of ketones are determined by their carbonyl group C=O with an unbonded electron pair at the oxygen atom. When the molecule absorbs a light quantum, one of the electrons of this pair can pass from the non-bonding $2p_y$ orbital to the antibonding π^* orbital ($n-\pi^*$ transition).



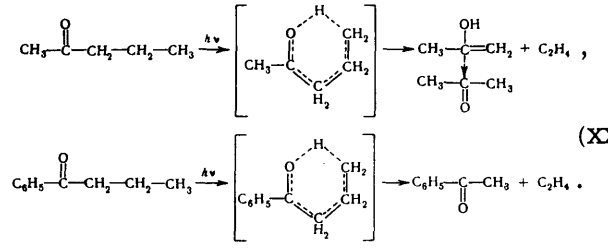
ground state n-π^* excited state (XXIV)

This transition is forbidden by symmetry and therefore the corresponding absorption band (in the region of 300 nm) is usually weak. The $\pi-\pi^*$ and $n-\sigma^*$ transitions are of course possible, but in aliphatic and many aromatic ketones the $n-\pi^*$ state is the lowest excited electronic state of the molecule. A second important characteristic of many ketones is the comparative ease of the intercombination transition of the excited molecule from the singlet to the triplet state. Since triplet states are usually much longer-lived than singlet states, this increases the likelihood that the molecule will enter into a chemical reaction. When one of the electrons of the pair is transferred from the n orbital to the π^* orbital, the interaction between the electrons is weakened and a structure resembling a free radical, with a shift of the negative charge to the carbonyl carbon atom, is generated in the carbonyl group. This is probably why carbonyl compounds in the excited state readily abstract hydrogen with formation of the O–H bond:



(XXV)

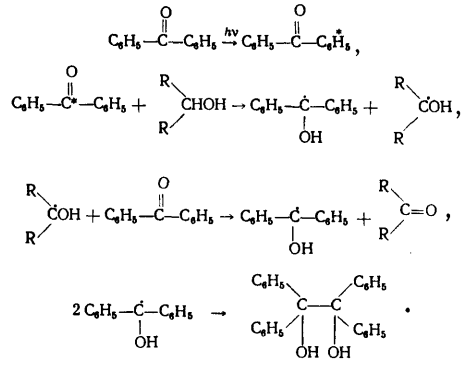
Hydrogen is abstracted both intermolecularly, for example from a solvent molecule, and intramolecularly, i.e. from a hydrogen-containing group of the ketone itself. The latter process takes place particularly readily if the ketone has an aliphatic substituent containing a hydrogen atom in the γ-position relative to the carbonyl group. Probably this proceeds via a stage involving the formation of a six-membered intermediate ring [54–56] and results in the elimination of an unsaturated compound from the ketone:



(XXVI)

Such "biting off of its own tail" by the excited ketone molecule is called Norrish type II split.

The most familiar photochemical reaction involving intermolecular abstraction of hydrogen by a ketone is the formation of benzopinacol from benzophenone, discovered by Ciamician and Silber [57] at the beginning of this century. Pitts and coworkers showed that reactions of this type involve the mechanism [58]



(XXVII)

The maximum possible quantum yield of the disappearance of the ketone in this reaction is 2.

Since the triplet $n-\pi^*$ state of benzophenone, which is the lowest excited electronic state, is involved in this reaction [59–62], it is important to consider to what extent the multiplicity and the nature of the state ($n-\pi^*$ or $\pi-\pi^*$) and the energy of excited molecules determine its capacity to enter into the hydrogen abstraction reaction.

The literature data [62] suggest that the involvement of excited singlet benzophenone molecules in the hydrogen abstraction reaction should be limited primarily by the short lifetime of these molecules [60]. This should be shown particularly clearly in cases where the rate of abstraction of hydrogen (k_r) is low compared with the rate of diffusion. Indeed the quantum yield of the abstraction of hydrogen is given in the simplest case by the expression

$$\varphi = \frac{k_r[B^*][RH]}{k_r[B^*][RH] + 1/\tau[B^*]}, \qquad \text{(XXVIII)}$$

where k_r is the rate constant for the abstraction of hydrogen, [B*] and [RH] are the concentrations of the excited benzophenone and hydrogen donor molecules and τ is the natural lifetime of B*. If it is supposed that the reactivities of excited singlet and triplet ketone molecules in the $n-\pi^*$ state are approximately the same, i.e. $k_r^{S_1} = k_r^T \simeq 10^6$ litre mole^{-1} s^{-1} [63] and $\tau_{S_1} \leq 10^{-9}$ s, then even for the reaction in pure alcohol {[RH] $\simeq$ 10 M}, φ for singlet molecules should be $\leq 10^{-2}$ while for triplet molecules $\varphi \simeq 1$ ($\tau_T \simeq 10^{-5}$ s). One should remember that the quantum yield of the singlet–triplet conversion is close to unity for benzophenone. Hence it is clear that virtually only the triplet benzophenone molecules should be involved in the reaction even if their reactivity is somewhat lower than that of the excited singlet molecules. The report that excited singlet molecules can also participate in hydrogen abstraction [64] was not confirmed [65].

We shall now consider to what extent the $n-\pi^*$ state determines the reactivity of ketones. As already mentioned, owing to the weak interaction between the n and π^* orbitals, the carbonyl group excited to the $n-\pi^*$ state behaves like a free radical. Walling and Gibian [66,67] compared the reactivities of the excited benzophenone molecule and the tetrabutoxy-radical with respect to different hydrogen donors (alcohols, unsaturated hydrocarbons, alkylbenzenes) and showed that the reactivities of the alkoxy-radical and the excited benzophenone molecule vary in parallel for the series of donors investigated, although the sensitivity of the excited molecule to the strength of the C–H bond of the donor is somewhat higher than that of the radical.

Ketones usually react in the lowest excited fairly long-lived triplet state. Therefore, as a result of a decrease of the $\pi-\pi^*$ excitation energy or an increase of the $n-\pi^*$ excitation energy, the $\pi-\pi^*$ state may become the lowest excited state or its contribution to the lowest excited state increases appreciably. Comparison of the decay times and the phosphorescence spectra of acetophenone and its mono- and di-methyl derivatives in different solvents leads to the conclusion that, with increase of the number of methyl groups in the benzene ring, the triplet level of the $n-\pi^*$ state becomes higher and that of the $\pi-\pi^*$ state becomes lower [68]. Accordingly, there is a sharp decrease also in the quantum yields of the reduction of ketones in 2-propanol and cyclohexane. However, one should note that, although the lowest triplet level in dimethylacetophenone is the $\pi-\pi^*$ state, pinacol is nevertheless formed with an appreciable quantum yield.

The same behaviour is observed on passing from acetophenone to acetonaphthone, i.e. when the benzene ring is replaced by a naphthalene ring [69]. In acetonaphthone the lowest triplet state is the $\pi-\pi^*$ state, which is not sufficiently reactive to abstract hydrogen from the alcohol. However, the reaction proceeds fairly readily with a stronger reducing agent—tri-n-butyl stannate.

Thus we see that transition from the $n-\pi^*$ to the $\pi-\pi^*$ state reduces significantly the reactivity of the excited ketone molecules in the hydrogen abstraction reaction, although the latter is not fully suppressed. This finding can probably be explained by the fact that in the $\pi-\pi^*$ excited state of the ketone there is always some contribution by the $n-\pi^*$ state.

Porter and Suppan [70] believe that the $\pi-\pi^*$ state "itself" has a definite reactivity in the photochemical reduction reaction. They believe that the experiment on the sensitised photochemical reduction of α-naphthaldehyde confirms this. The lowest triplet level of this substance is the $\pi-\pi^*$ state (19 900 cm^{-1}), which lies below the triplet $n-\pi^*$ level by more than 3000 cm^{-1}. The lowest $\pi-\pi^*$ level was populated by the transfer of excitation energy from 4,4′-[N(CH$_3$)$_2$PhCO]$_2$, the lowest triplet level of which is near 21 700 cm^{-1}. It was found that with such selective population of the triplet $\pi-\pi^*$ state of α-naphthaldehyde, the quantum yield of the photochemical reduction is appreciably higher than on direct excitation of the aldehyde. However, it is then evidently difficult to assert that the lowest level is a "pure" $\pi-\pi^*$ level.

When electron-donating substituents [NH$_2$, N(CH$_3$)$_2$, OH] are introduced into the *para*-position of the benzene ring of benzophenone, the quantum yield of the photochemical reduction decreases sharply [26]. Porter and coworkers [65,70] showed that this is caused by the generation of a charge-transfer state (CTS), which leads to the disappearance of the electron density deficit at the carbonyl oxygen in the excited state. Moreover, in these excited molecules the negative charge is displaced towards the carbonyl oxygen:



(XXIX)

This leads to a sharp decrease of the reactivity of these molecules in electrophilic attack (the abstraction of the hydrogen atom may be regarded as successive removal of an electron and then a proton from the hydrogen donor [65]).

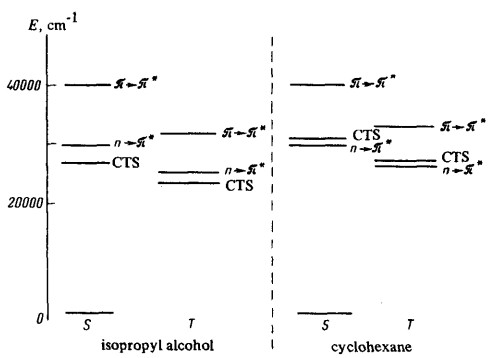


Figure 9. Energy levels of *p*-aminobenzophenone in isopropyl alcohol and cyclohexane [65].

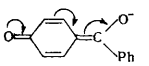
Porter [65,70] regards the $\pi-\pi^*$, $n-\pi^*$, and charge-transfer states in compounds of the type of *p*-aminobenzophenone as separate excited levels with different reactivities. On passing from a polar solvent (isopropyl alcohol) to a non-polar solvent (cyclohexane), the polarising influence of the solvent diminishes and the lowest triplet state becomes $n-\pi^*$ and not the charge-transfer state (see scheme in Fig. 9). The quantum yield of the disappearance of aminobenzophenone increases accordingly from zero in isopropyl alcohol to 0.2 in cyclohexane.

The comparison of hydroxy- and methoxy-benzophenones is extremely interesting. The complete similarity of the spectra of these compounds suggests that they have approximately the same distribution of levels and the short phosphorescence decay times in hydrocarbon and alcoholic matrices indicate that the lowest triplet level in both substances is the $n-\pi^*$ state. Nevertheless methoxybenzophenone reacts in isopropyl alcohol with a quantum yield $\varphi \simeq 1$ and hydroxybenzophenone reacts with $\varphi = 0.02$.

Porter and Suppan [70] believe that hydroxybenzophenone exhibits acidic properties in the excited state:

$$H—O—Ph_2CO \rightleftharpoons {}^{-}O—Ph_2CO + H^{+} .$$

The anion formed is unreactive in isopropyl alcohol since now the lowest triplet level is the charge-transfer state.



(XXX)

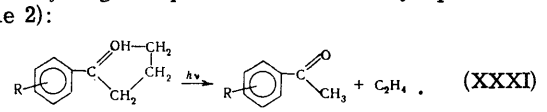
In cyclohexane, where there is no stabilisation of the charge-transfer state by the solvent, hydroxybenzophenone reacts with a quantum yield close to unity.

The properties of various excited states of the benzophenones studied by Porter and Suppan are summaried in Table 1.

Table 1. The properties of the $n-\pi^*$, $\pi-\pi^*$, and charge-transfer states of benzophenone derivatives.

States	Intensity of light absorption, lg ε	Energy range (cm^{-1} in *para*-derivatives)	Shift of absorption band by solvent, cm^{-1}	T-S splitting, cm^{-1}	Reactivity φ	Lifetime in triplet level, ms	Distribution of electrons in carbonyl group
$n-\pi^*$	2	30 000	−800	<3000	1	< 20	$C=O^{\delta+}$
$\pi-\pi^*$	4	40 000	+600	10 000	0.1	>100	C=O
CTS	3—4	30 000	+2500	>3000	0.01	>100	$C=O^{\delta-}$

Pitts and coworkers [62,71,72] believe that the unreactive state in the *para*-substituted benzophenones discussed is the triplet $\pi-\pi^*$ state (the charge-transfer state is not considered as such, as it is believed that it only makes a contribution to the $\pi-\pi^*$ state). Baum et al. [71] compared the quantum yields of the intramolecular photochemical abstraction of hydrogen in *para*-substituted butyrophenones (Table 2):



(XXXI)

Table 2. The quantum yields (φ_{II}) of the Norrish type II photochemical cleavage in benzene solutions at 25°C and 313 nm.

Butyrophenone derivatives substituted in the *para*-position	φ_{II}	Triplet level, kcal	Butyrophenone derivatives substituted in the *para*-position	φ_{II}	Triplet level, kcal
p-Cl	0.43	72.4	*p*-OH	0.00	71.0
p-$OCOCH_3$	0.42	74.3	*p*-NH_2	0.00	64.5
p-H	0.42	74.7	*p*-$NHCOCH_3$	0.00	69.9
p-CH_3	0.39	73.7	*p*-C_6H_5	0.00	not established
p-F	0.29	72.9	*p*-Br	0.00	72.9
p-OCH_3	0.10	73.3			

The data in Table 2 agree with data for the intermolecular photochemical reduction of benzophenone: as the electron-donating properties of the substituent become more pronounced, the reactivity diminishes. As before, this can be explained by a transition from the lowest $n-\pi^*$ state to the $\pi-\pi^*$ state, which involves an increase of the negative charge at the carbonyl oxygen.

It is interesting that, on passing from isopropyl alcohol to cyclohexane, there is no significant change of φ_{II}. The solvent behaves merely as a medium and its polarity evidently does not influence the rate of reaction. Clearly this result is inconsistent with Porter's data. (Pitts [71,73] notes that pinacol could not be detected at all in the photochemical reaction of *p*-aminobenzophenone in cyclohexane.)

Yang and Dusenbery [74] compared the rate constants for the photochemical abstraction of hydrogen by acetophenone and its derivatives [*p*-CH_3, *p*-CF_3, 3,4-$(CH_3)_2$] with the positions of the $[\pi-\pi^*]^1$, $[\pi-\pi^*]^3$, $[n-\pi^*]^1$, and $[n-\pi^*]^3$ levels in these compounds. It was found that the introduction of the electron accepting *p*-CF_3 group into acetophenone increases the distance between the $[\pi-\pi^*]^1$ and $[n-\pi^*]^3$ levels, which reduces the contribution of the $[\pi-\eta^*]^1$ state to the lowest state $[\pi-\eta^*]^3$ and increases the rate of photochemical abstraction of hydrogen. Introduction of the electron-donating CH_3 groups decreases the vibronic interaction of the $[\pi-\pi^*]^3$ level (which in this case is the lowest excited level) with the $[n-\pi^*]^3$ level and thereby reduces its reactivity.

In many compounds the $n-\pi^*$ and $\pi-\pi^*$ levels are so close that it is difficult to tell which of them in fact reacts.

In a study of the photochemical cleavage of substituted butyrophenones, Pitts and coworkers [75] compared the φ_{II} for these substances with their phosphorescence decay times in a solid matrix and found that for certain compounds, for example for *ortho*- and *para*-acetoxy-derivatives, the phosphorescence decay time and hence the contribution of the $[\pi-\pi^*]^3$ state to the lowest $[n-\pi^*]^3$ state increase sharply. At the same time the φ_{II} for these compounds have the same value as for the unsubstituted ketone (~ 0.4). This contradiction may arise because, for a constant quantum yield, the photochemical reaction rate constants may diminish significantly, as was shown for substituted valerophenones [76,77]. In this connection one must emphasise yet again that a simple comparison of the reaction quantum yields can lead to incorrect conclusions, since the quantum yield is not determined solely by the photochemical reaction rate constant but also by the lifetime of the excited molecule. It has been shown that in many cases [78,79] an increase of the contribution of the charge-transfer state to the excited state entails a decrease of the lifetime of the excited molecules.

In a discussion of the mechanism of hydrogen abstraction by ketones, the problem arises whether this reaction should be regarded as a two-stage process (electron and then proton transfer from the alcohol) or a single-stage process (radical abstraction of the hydrogen atom). In the first case heterolytic electrophilic substitution is evidently the rate-limiting stage, while in the second stage the reaction is homolytic. The available experimental data are insufficient to resolve this problem, which is important for the construction of a model of the transition state in the reaction.

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