

REACTIVITY OF EXCITED STATES OF AROMATIC KETONES

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INTRODUCTION

In the spectroscopy of organic molecules it has proved a useful approximation to classify electronically excited states in terms of the electron configuration which makes the major contribution to that state. Some of the most important configurations are those described as $\pi\text{-}\pi^*$, $n\text{-}\pi^*$, $n\text{-}\sigma^*$ and, as we shall see later, charge transfer (C-T). In addition each of these configurations may give rise to a singlet or a triplet state.

The question which we wish to consider in this paper is to what extent the photochemical behaviour of molecules can also be predicted from the type of electronic excitation. We shall not be concerned with small quantitative differences which will clearly require exact quantitative calculations of electron distributions but with major qualitative differences in reactivity.

The photochemistry of large molecules, particularly in solution, is greatly simplified by the fact that radiationless processes are almost invariably so rapid that the lowest excited singlet and triplet states are reached before reaction begins, so that only these two states need to be considered¹. In a comparative study of the reactivity of different states, however, this is a great restriction since, in a single molecule under given conditions, we can study at the most two states, and usually only one. Fortunately, it is possible to shift the relative energies of excited states in two ways, by substitution in the molecule itself and by external solvent perturbation. This is true of carbonyl compounds and particularly of aromatic carbonyls which have been very extensively studied and which provide an excellent system for the study of comparative reactivities in excited states.

Even in the simplest carbonyl compounds, such as formaldehyde for example, four excited electronic states must be considered: $n\text{-}\pi^*$ (triplet), $n\text{-}\pi^*$ (singlet), $\pi\text{-}\pi^*$ (triplet) and $\pi\text{-}\pi^*$ (singlet), this being the order of increasing energy in aldehydes and ketones. Other generalizations which are usually applicable are that the singlet-triplet splitting of $n\text{-}\pi^*$ states is small compared with that of $\pi\text{-}\pi^*$ states, the natural lifetime of triplet states with respect to radiative conversion to the ground state is much greater than that of singlet states and thirdly, in hydrogen bonding solvents such as water and alcohols, the excitation energy of $n\text{-}\pi^*$ states is increased (blue shift) whilst that of $\pi\text{-}\pi^*$ states is decreased (red shift).

It is important to define chemical reactivity in terms of rate constants of reaction of the separate states rather than in terms of the contribution of each state to the overall reaction. It is usually found, for example, that the

bimolecular reactions of carbonyl compounds occur *via* the triplet state. This does not imply immediately that the electronic distribution in the triplet state is such that its reactivity is intrinsically greater than that of the singlet. Conversion from the excited singlet to the triplet may occur in a time of 10^{-7} sec or less in solution and, since the natural radiative lifetime of the triplet is several milliseconds, a factor of approximately 10^4 is to be expected in their relative contributions to chemical reaction even if the intrinsic reactivities or rate constants of the two states are equal. This factor is so large that few experiments are able to detect reactivity of the singlet state if the triplet is populated. There is no doubt that the electronic distribution in the lowest excited singlet (S_1) and triplet (T_1) states of the same molecule is often significantly different as illustrated by the widely different acidity constants in the S_1 and T_1 states of molecules such as naphthol and naphthylamine². In one case, one of the earliest which was studied in detail, reaction appears to go *via* the singlet state³, but in most cases reaction occurs predominantly through the triplet. Little is known experimentally about relative reactivities of singlets and triplets, although certain generalizations are possible on theoretical grounds.

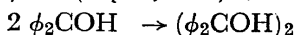
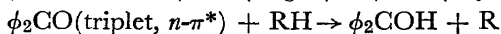
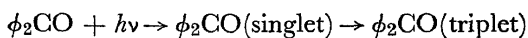
In most aldehydes and ketones distinction between the intrinsic reactivities of the $n-\pi^*$ and $\pi-\pi^*$ states cannot be made for the same reason; conversion to the lowest level is extremely rapid and, since this is usually an $n-\pi^*$ triplet of long life, reaction occurs exclusively *via* this state. In many aromatic aldehydes, ketones and quinones, however, both the absolute and relative energies of these levels may be changed either by substitution or by solvent perturbation.

The effect of substituents on the photochemical reduction of quinones to hydroquinones³ and of aromatic ketones to pinacols in alcoholic solution has been known for some time and several authors have interpreted these effects qualitatively in terms of the relative positions of $n-\pi^*$ and $\pi-\pi^*$ levels^{4, 5}. None of these explanations has been entirely convincing because of the numerous exceptions and anomalies and they become even less satisfactory when an attempt is made to incorporate the spectroscopic data into the picture. We have recently completed a detailed study of benzophenone and its derivatives as a result of which a rather complete interpretation of the effect of substituents, both on electronic energy levels and chemical reactivity, can be given. Some of the preliminary work has already been published⁶⁻⁷ and details of our recent work will be published shortly. In this communication therefore we shall only summarize the principal results and conclusions.

THE PHOTOCHEMISTRY OF BENZOPHENONES

Like most carbonyl compounds, benzophenone upon optical excitation in solution, is converted to the lowest triplet state in less than 10^{-7} sec with a quantum yield near unity. The lowest triplet state is of $n-\pi^*$ type and therefore the oxygen atom in this state is electron-deficient. The $n-\pi^*$ triplet state rapidly reacts with reducing agents by abstracting either an electron or an electron plus proton (a hydrogen atom) from the solvent giving a ketyl radical which, in the absence of other reactants dimerises to give the pinacol^{8, 9}.

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There are secondary reactions which may result in quantum yields of pinacolization greater or less than unity but these are not relevant to the present discussion. Furthermore, the ketyl radical may exist in acidic or basic forms depending on the pH of the solution⁵. This has a profound effect on the rate of the secondary reactions and results in the appearance of a stable radical in strongly alkaline solutions.

SUBSTITUTED BENZOPHENONES

ortho-Substituted ketones, or those with other substituents which can form a six-membered ring, hydrogen-bonded to the carbonyl oxygen, tautomerize undergoing the intramolecular equivalent of the hydrogen abstraction from the solvent. The tautomer reverts rapidly to the original ketone but may be detected by its addition reactions¹⁰ or may be observed directly by means of its absorption spectrum for a few seconds following flash photolysis⁵. Alkyl and amino groups are effective in preventing reaction with the solvent when substituted in the *ortho* position. This interesting reaction is discussed in other communications at this meeting and is not relevant in the present context.

The most striking effect of substituents on the photochemistry of aromatic aldehydes and ketones, and the one which is of particular interest in connection with studies of the relative reactivities of different electronic states is the effect of OH, NH₂ and similar groups substituted in the *para*, and to a lesser extent in the *meta* position. These two substituents reduce the quantum yield of pinacolization of benzophenones in alcoholic solution from unity to nearly zero. In view of the hydrogen bonding effects which occur in the *ortho* position it is natural to attribute this to dimer formation involving two hydrogen bonds between two molecules, but molecular weight and spectroscopic studies have eliminated this possibility⁵. Attempts to explain these phenomena in terms of shifts of *n*- π^* and π - π^* levels met with partial success^{4, 5} but created almost as many problems as they answered. Some of the difficulties in this type of explanation are as follows:—

(i) N(CH₃)₂, NH₂ and OH substitution in the *para* position are effective in preventing reaction but OCH₃ has no effect.

(ii) *para*-OCH₃ and OH derivatives have almost identical spectra.

(iii) *para*-Phenylbenzophenone, which spectroscopically is seen¹¹ to have a lowest triplet which is π - π^* , has a relatively high reactivity (quantum yield 0.1) compared with *para*-OH and NH₂ derivatives.

(iv) The π - π^* band of benzophenone is at 250 $\mu\mu$, and an absorption band of the same intensity is present at nearly the same wavelength (245 $\mu\mu$) in *o*-NH₂- ϕ_2 CO, *m*-NH₂- ϕ_2 CO, *p*-NH₂- ϕ_2 CO, *pp'* (NMe₂)₂- ϕ_2 CO, etc. while the long-wavelength absorption band in these compounds varies considerably both in position and in intensity. The interpretation of the long-wavelength bands as being the π - π^* (250 $\mu\mu$) band of benzophenone shifted to lower energy cannot therefore be taken for granted.

Other observations which are relevant are that all these *para*-substituted derivatives phosphoresce strongly in low temperature solutions showing that the triplet state is populated in all cases; the acidity constant of *p*-OH benzophenone is 6.5 but the molecule is unreactive with alcohols in solutions of pH between 1 and 13.

THE IMPORTANCE OF CHARGE TRANSFER STATES

The clue to these problems is provided by a more detailed examination of the emission and absorption spectra of benzophenone derivatives and the influence of solvent on these spectra. *Figure 1* compares the absorption spectrum of benzophenone with that of *p*-aminobenzophenone in both hydroxylic (isopropanol) and hydrocarbon (cyclohexane) solvents. It will be seen that:

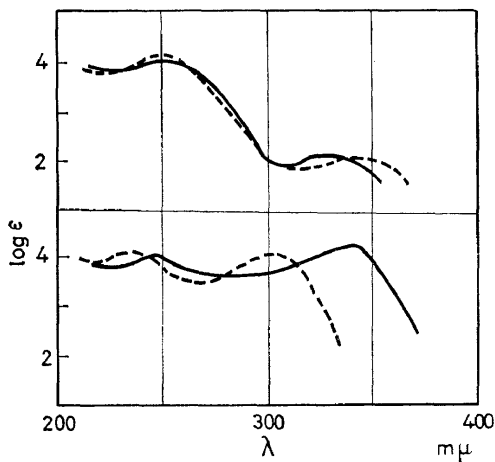


Figure 1. Absorption spectra of ϕ_2CO and $4-NH_2-\phi_2CO$

(a) Benzophenone shows the well-known weak $n-\pi^*$ band at 340 $m\mu$ and the strong $\pi-\pi^*$ band at 250 $m\mu$ which show shifts of -1000 cm^{-1} and $+600\text{ cm}^{-1}$ respectively on passing from a hydroxylic to a hydrocarbon solvent. Chlorine and bromine substitution has little effect on these transitions other than to produce a slight shift of the $\pi-\pi^*$ band to longer wavelengths.

(b) In *p*-aminobenzophenone the $\pi-\pi^*$ band is unchanged apart from a very small hypsochromic shift. On the other hand a very strong ($\epsilon_{\max} = 20,000$) new absorption band appears at longer wavelengths. This band is not present in aniline or benzophenone and for this and other reasons to be given presently, we shall refer to it as the charge-transfer band.

If we represent *p*-aminobenzophenone by the formula DRA where D is the electron-donating amino group, R is the aromatic ring and A is the electron-accepting carbonyl group, the important charge transfer states are D^+R^-A corresponding to the charge transfer state of aniline, DR^+A^- corresponding to the charge transfer state of benzophenone and D^+RA^- which is, of course, only possible in the aminobenzophenone itself. These

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three states interact with each other¹² (but not with locally excited states DR*A) to give the low energy state which is observed and which we propose to call simply the charge-transfer (C-T) state. It is to be regarded as a new state and has little connection with the states which give rise to the $n-\pi^*$ and $\pi-\pi^*$ transitions in benzophenone.

The charge-transfer character of this state must result in a large dipole moment and this is borne out by the striking effect of solvent on the energy of the transition ($+3000\text{ cm}^{-1}$). The negative charge on the oxygen in this state is the opposite of the electronic situation in the $n-\pi^*$ state and we shall expect reactivities of $n-\pi^*$ and C-T states to differ greatly and to be respectively greater and less than the reactivity of $\pi-\pi^*$ states for electron or hydrogen atom abstraction by the carbonyl group.

POSITIONS OF TRIPLET LEVELS

All these derivatives phosphoresce so that the positions of their lowest triplet levels are readily obtained. The principal conclusions from these studies are as follows:

(i) Singlet-triplet splitting of C-T states is much smaller than that of $\pi-\pi^*$ states and similar to that of $n-\pi^*$ states.

(ii) Triplet lifetimes of C-T states are much longer than those of $n-\pi^*$ states, (e.g. 200 msec for *p*-aminobenzophenone compared with 5.4 msec for benzophenone).

By combination of absorption and emission data energy level diagrams can now be constructed and one of these, for *p*-aminobenzophenone is shown in Figure 2.

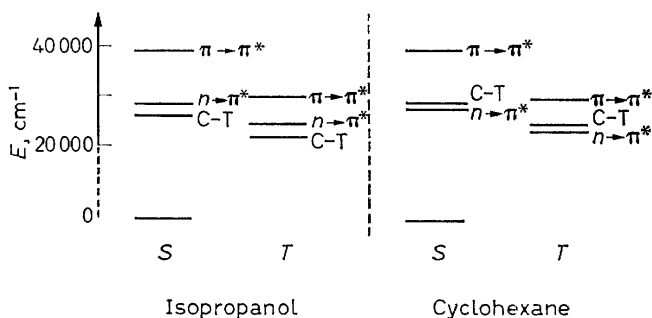


Figure 2. Energy levels of 4-NH₂-benzophenone

QUANTUM YIELDS OF PINACOLIZATION

The results of these measurements have already been referred to and, with the exception of *p*-OH benzophenone which will be treated separately, comparison of these yields with the energy levels derived spectroscopically leads to the following conclusions:

(i) When the lowest triplet level is $n-\pi^*$, quantum yields of pinacolization are near to unity.

(ii) In the one example where the lowest triplet level is $\pi-\pi^*$ (*p*-phenylbenzophenone) the quantum yield is 0.1. (In this molecule the lowest excited singlet is $n-\pi^*$).

(iii) When the lowest triplet level is C-T the quantum yield of pinacolization is zero (less than 0.01).

These results are exactly in accordance with prediction based on the electron distribution in the three states.

EFFECT OF SOLVENT

The energy level diagram in *Figure 2* leads to the prediction of a striking effect. It will be seen that the great effect of polar solvents on the C-T state band results in this being the lowest in hydroxylic solvents but not in hydrocarbons where the $n-\pi^*$ state is of lower energy. We therefore, predict that *p*-amino benzophenone should abstract hydrogen from paraffins but not from alcohols in complete contrast to all chemical expectations. This is found to be the case, not only for *p*-amino- but also for *p*-hydroxy- and *p,p'* (NMe₂)₂- benzophenone, the quantum yields being 0.2, 0.9 and 0.6 respectively for reaction with cyclohexane, and zero for reaction with isopropanol.

The "anomalous" case of *p*-hydroxy benzophenone

The spectra and energy levels of *p*-OH and *p*-OCH₃ benzophenones are nearly identical and show that both have lowest triplet levels of $n-\pi^*$ type and should, therefore, be reactive. This is true for the *p*-OMe derivative but not for *p*-OH benzophenone which has nearly zero (0.02) quantum yield in isopropanol. An immediate explanation would be possible if the substituent were in fact in the basic form, *p*-O⁻ benzophenone, since, the O⁻ substituent is known to be a very strong donor. This is borne out by studies of the absorption spectra in alkaline solution where the C-T band appears at wavelengths longer even than in the *p*-amino derivative (*Figure 3*).

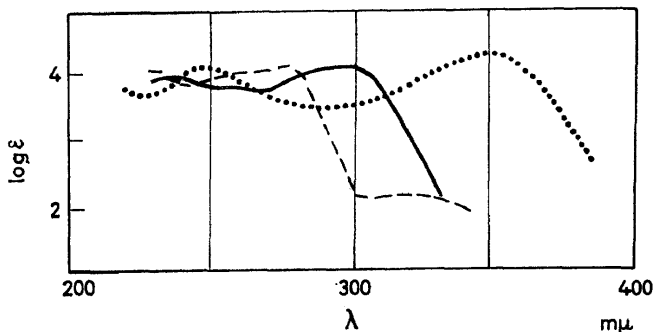


Figure 3. Absorption spectra of 4-OH-benzophenone

— in alcohol
 ---- in paraffin
 4.0- ϕ_2 CO

However, this explanation, as it stands, is inadequate since the *pK* of this protonation equilibrium is 6.5 yet the *p*-hydroxybenzophenone is unreactive at all pH's between 1 and 13.

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If the pK were very much lower in the excited states an explanation would be given immediately since the molecule would react in the unprotonated form. We have estimated the pK in both the excited singlet and triplet states from the spectra¹³ and find that it is in fact profoundly changed, the constants being $pK_S^* = -4$, $pK_T = 3.5$. This not only removes the anomaly but provides another example of how the reversal of energy levels changes the reactivity. It may be noted that the extremely low pK in these excited states is exactly what would be expected of the charge transfer state.

FLASH PHOTOLYSIS RESULTS

Flash photolysis studies on these benzophenone derivatives, carried out in collaboration with Dr T. Godfrey result in the detection of transients which may be attributed to ketyl radicals, triplet states and changes of the state of protonation. The appearance of these species from the different derivatives and in different solvents fully confirms the conclusions given in this paper, and will be reported elsewhere. Studies on acetophenones and benzaldehydes indicate that similar arguments apply also to these compounds.

In these aromatic ketones we have, therefore, a series of compounds whose lowest electronic states differ very little in energy but differ profoundly in electron distribution and consequently in reactivity. Their varied photochemistry is now almost completely predictable solely on the basis of spectroscopic measurements (*Table 1*).

Table 1. Electronic excitations of aromatic carbonyls

State	Intensity (log ϵ) (in <i>p</i> -subst.)	Energy range (cm^{-1}) (in <i>p</i> -subst.)	Solvent shift (cm^{-1}) (in <i>p</i> -subst.)	T-S splitting (cm^{-1})	Reactivity (Φ)	Triplet lifetime, 77°K (msec) (in <i>p</i> -subst.)	Electron distrib- ution
$n \rightarrow \pi^*$	2	30 000	-800	<3000	1	<20	$\text{>C=O}^{\delta+}$
$\pi \rightarrow \pi^*$	4	40 000	+600	10000	0.1	>100	>C=O
C-T	4	30 000	+2500	>3000	0.0	>100	$\text{>C=O}^{\delta-}$

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