THE PERTURBATIONAL TREATMENT OF THE PROCESS OF HYDROGEN ABSTRACTION BY KETONES

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Summary

The change in energy during hydrogen abstraction by ketones is estimated for different electronic states as a function of the intermolecular orbital overlap employing perturbation theory. The results suggest that ketones preferentially undergo the in-plane reaction and abstract a hydrogen atom in their triplet $n\pi^*$ state. For ketones where the triplet $\pi\pi^*$ state lies below the triplet $n\pi^*$ state, hydrogen abstraction can take place in the $\pi\pi^*$ state owing to the crossing of the zero order reaction surfaces of the $n\pi^*$ and $\pi\pi^*$ states.

1. Introduction

Chemical reactions are usually discussed in terms of either correlation diagrams [1, 2] or perturbation theory [3, 4]. However, perturbation theory is central to any theory of chemical reactivity because it can be shown that the perturbation approach leads to the Woodward–Hoffmann symmetry rules [4] which were derived from correlation diagrams. The construction of correlation diagrams requires a knowledge of the symmetries and energies of the orbitals of both reactants and products. In contrast, in the perturbation approach, the symmetries and energies of the orbitals of the reactants alone need to be known.

Perturbation theory is a natural procedure for estimating the interaction energy when two reacting systems interact weakly and the total perturbation energy is therefore a measure of the initial slope of the reaction profiles [4]. Hudson [4] has further shown that the perturbation energy can determine the reaction path for a series of similar reactions if the chemical non-crossing rule [5] holds. Since this condition is satisfied in most photochemical and in some thermal reactions [4, 6], we shall follow the perturbation approach in the study of the photochemical abstraction of hydrogen atoms by ketones.

Ketones in their lowest triplet $n\pi^*$ state abstract hydrogen atoms by an intermolecular process [7] as well as by an intramolecular (Type II) photo-

elimination process (γ hydrogen abstraction). The lowest triplet $n\pi^*$ states are generally involved in these reactions. There are, however, some ketones, such as 4-methyl acetophenone and some substituted phenyl alkyl ketones whose lowest electronic states are characterized empirically as triplet $\pi\pi^*$ states, which also undergo hydrogen abstraction [8 - 10]. The rate constants for abstraction by these $\pi\pi^*$ triplet ketones are an order of magnitude smaller than that for acetophenone which abstracts a hydrogen atom in its lowest triplet $n\pi^*$ state under similar conditions. The main objective of this paper is to show how perturbation theory at the semi-empirical level provides a mechanism for the hydrogen abstraction process initiated in the $n\pi^*$ or in the $\pi\pi^*$ state of ketones.

2. Theory

We shall follow the intermolecular perturbation theory with overlap which has been worked out in detail by Salem [11], Murrell et al. [12] and Imamura [13]. Our analysis therefore has no new theoretical features. We assume no change in the nuclear geometry of the reactants accompanying chemical reaction and therefore no first order change in the energy of the reactant orbitals. These are important for the chemical "non-crossing rule" to be valid.

Usually, the interacting orbitals in the hydrogen abstraction process are non-degenerate. For the reaction between a carbonyl group and a carbon–hydrogen bond, the relevant orbitals are the oxygen lone pair orbital n_O and the π and π^* orbitals of the ketone and the σ and σ^* orbitals of the carbon–hydrogen bond of the hydrogen donor. We shall first consider the in-plane reaction between a ketone and a C–H bond of a hydrogen donor. If the carbonyl group and the C–H bond are coplanar with π and π^* orbitals sticking out of the plane, as shown in Fig. 1, then for the in-plane reaction the n_O and σ orbitals only are perturbed, while the interaction between the π orbitals of a ketone and the σ orbitals of the hydrogen donor is forbidden by symmetry. The change in energy of the n_O and σ orbitals is given by

$$\Delta E^{(2)}(n_O) = \frac{\{\langle n_O|H|\sigma\rangle - S(n_O\sigma)E(n_O)\}^2}{E(n_O) - E(\sigma)} + \frac{\{\langle n_O|H|\sigma^*\rangle - S(n_O\sigma^*)E(n_O)\}^2}{E(n_O) - E(\sigma^*)} \tag{1}$$

$$\Delta E^{(2)}(\sigma) = \frac{\{\langle n_O|H|\sigma\rangle - S(n_O\sigma)E(\sigma)\}^2}{E(\sigma) - E(n_O)} \tag{2}$$

where H is the total hamiltonian of the composite system, E the energy and S the overlap of the participating orbitals. Since, within the framework of the extended Hückel theory [14], the two-electron terms are taken in an effective way into the hamiltonian, the total energy of a given state is a simple sum of the orbital energies multiplied by their appropriate occupation numbers, because the nuclear–nuclear repulsion terms approximately cancel
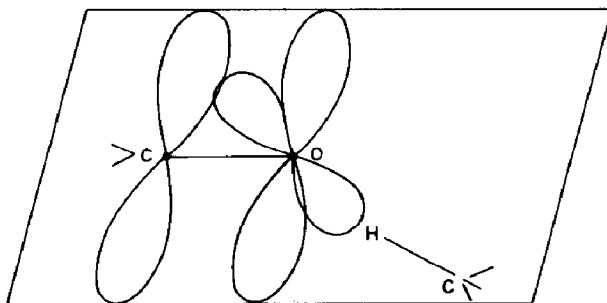
Fig. 1. In-plane interaction of the carbonyl group of a ketone and the C—H bond of a hydrogen donor. All four atoms are in the same plane.

the electron—electron repulsion terms. We therefore assume that the total change in energy during the reaction is approximately given by

$$\Delta E = n\Delta E^{(2)}(\mathrm{n_O}) + 2\Delta E^{(2)}(\sigma) \tag{3}$$

where n is the occupation number of the lone pair orbital in the various electronic states of the ketone. For example, $n = 2$ for the ground and $\pi\pi^*$ states and $n = 1$ for the $n\pi^*$ state of the ketone. The quantities of $\Delta E^{(2)}(\mathrm{n_O})$ and $\Delta E^{(2)}(\sigma)$ are given by eqns. (1) and (2) respectively.

If the reaction takes place in a perpendicular plane passing through the oxygen atom of the carbonyl group, as shown in Fig. 2, the lone pair orbital remains unaffected while all the π and π^* orbitals that have finite amplitudes on the oxygen atom interact with the σ and σ^* orbitals of the hydrogen donor. The change in energy of a π_i orbital of a ketone and that of the σ orbital of the C—H bond is given by

$$\Delta E^{(2)}(\pi_i) = \frac{\{\langle \pi_i|H|\sigma\rangle - S(\pi_i\sigma)E(\pi_i)\}^2}{E(\pi_i) - E(\sigma)} + \frac{\{\langle \pi_i|H|\sigma^*\rangle - S(\pi_i\sigma^*)E(\pi_i)\}^2}{E(\pi_i) - E(\sigma^*)} \tag{4}$$

$$\Delta E^{(2)}(\sigma) = \sum_i \frac{\{\langle \pi_i|H|\sigma\rangle - S(\pi_i\sigma)E(\sigma)\}^2}{E(\sigma) - E(\pi_i)} \tag{5}$$

where i denotes all the π orbitals of the ketone, occupied and unoccupied. Therefore, for the perpendicular plane reaction involving a ketone and a C—H bond of a hydrogen donor, the total change in the energy during the reaction will be approximately given by

$$\Delta E = \sum_i n_i \Delta E^{(2)}(\pi_i) + 2\Delta E(\sigma) \tag{6}$$

where n_i is the occupation number of the ith π orbital in the various electronic states of the ketone and $\Delta E^{(2)}(\pi_i)$ and $\Delta E^{(2)}(\sigma)$ are given by eqns. (4) and (5) respectively.

2.1. Evaluation of the matrix elements

For the evaluation of the matrix elements appearing in equations (1), (2), (4) and (5), we shall define the total hamiltonian as [11]
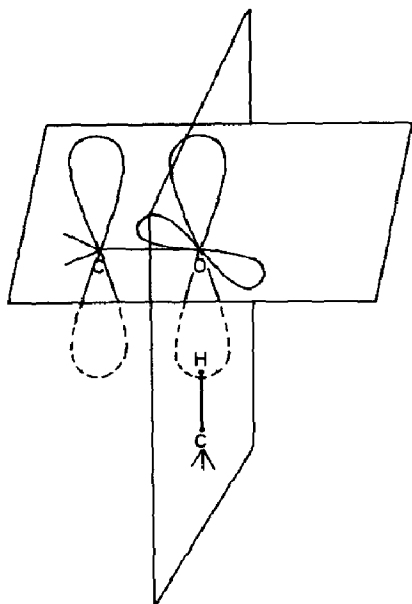
Fig. 2. Perpendicular plane interaction of the carbonyl group with the C—H bond of a hydrogen donor.

$$H = t + v + v'$$ (7)

where t is the kinetic energy operator and v and v' refer to some average potential fields of the two molecules. The integral $\langle \phi_i | H | \phi_{j'} \rangle$, where ϕ_i and $\phi_{j'}$ are the molecular orbitals of the two component molecules, is given by

$$\langle \phi_i | H | \phi_{j'} \rangle = \tfrac{1}{2}(E_i + E_{j'})S_{ij'} + \langle \phi_i | V | \phi_{j'} \rangle$$ (8)

where

$$V = \tfrac{1}{2}(v + v')$$ (9)

V is large only in the region between the two molecules. We assume that the operator V is an effective one-electron operator, so that the matrix elements of V over molecular orbitals localized in the same molecule are treated as zero while those of V over the molecular orbitals of both the molecules can be determined by semi-empirical means. Such approximations imply that two-electron repulsive effects are not treated explicitly and therefore such procedures cannot reveal certain subtle features in the reactions, such as the height of the barriers, the formation of intermediates etc., during the course of reactions. But they certainly reveal whether a given reactive state is progressively stabilized or destabilized as the reaction proceeds. Therefore plots of the total interaction energy *versus* the reaction coordinate should provide information about the initial slope of the correct reaction profiles. This is strongly indicated by the success of perturbation theory in predicting diverse reactivity trends of thermal [15, 16] and photochemical [17] reactions.

Since the reaction between a ketone and a hydrogen donor takes place through an interaction between the oxygen 2p orbital ϕ_O and the hydrogen 1s orbital ϕ_H, the integral $\langle \phi_i|V|\phi_j \rangle$ essentially involves $\langle \phi_O|V|\phi_H \rangle$. This integral is negative because the major effect is the attractive nuclear field and will again be proportional to the overlap S of the participating orbitals. There is no unique way to evaluate this proportionality constant and it is not likely to be the same for the wide range of the internuclear separations.

According to the semi-empirical procedure of Hoffmann [14], the integral $\langle \phi_O|H|\phi_H \rangle$ for an O—H bond is given by

$$\langle \phi_O|H|\phi_H \rangle = (1.75/2)(U_O + U_H)S = -27.1S \tag{10}$$

where U_O and U_H are the valence state ionization potentials (eV) of the oxygen 2p and hydrogen 1s orbitals. Using the definition of H given in eqn. (7) and ignoring the kinetic energy term in the hamiltonian we can write

$$\langle \phi_O|V|\phi_H \rangle = \tfrac{1}{2}\langle \phi_O|H|\phi_H \rangle = -13.5S \tag{11}$$

The Hückel-type resonance integral terms also appear in the off-diagonal matrix elements of the F matrix in complete neglect of differential overlap theory. According to Pople and Segal [18], the integral $\langle \phi_O|H|\phi_H \rangle$ for an O—H bond in a molecule is given by

$$\langle \phi_O|H|\phi_H \rangle = \tfrac{1}{2}(\beta_O^0 + \beta_H^0)S \tag{12}$$

where the parameters β^0 for the various atoms are chosen so as to reproduce the results obtained from *ab initio* calculations. Ignoring the kinetic energy term in the hamiltonian and employing the values of β^0 from ref. 18 the integral $\langle \phi_O|V|\phi_H \rangle$ is given by

$$\langle \phi_O|V|\phi_H \rangle = \tfrac{1}{2}\langle \phi_O|H|\phi_H \rangle = -10S \tag{13}$$

This shows that in the approximation $\langle \phi_O|V|\phi_H \rangle \sim KS$ the value of K lies between -10 and -14 eV when the separation between the two atoms is of the order of the chemical bond.

The electrostatic interaction E_{el} between two molecules is usually expressed in terms of the multipole expansion [19] as

$$E_{el} = E(q_A q_B) + E(q_A \mu_B) + E(q_A Q_B) + \ldots E(\mu_A \mu_B) \tag{14}$$

where q, μ and Q, ... denote respectively the point charges, dipoles and quadrupoles etc., and the energy terms depend respectively on $1/R$, $1/R^2$ etc. where R is the distance between the two molecules. When R is small the convergence of equation (14) is slow and hence a large number of terms are needed to get a good approximation. When R is very large, the first term is sufficient for the correct description of the electrostatic interaction. This implies that for a large value of R, and hence for a very small value of S, the proportionality constant K for the matrix element $\langle \phi_O|V|\phi_H \rangle$ is likely to be smaller than that prescribed for the bond distance. Salem [11] has chosen $K = -3$ eV in the calculation of the interaction energies between the two carbon 2p orbitals for R greater than the C—C bond distance. The calculated interaction energies [20] between two ground state pyrene

molecules in the symmetric sandwich conformation at a distance of 3–4 Å agree with the observed values [21] for $K \approx -1$ eV. We therefore presume that the value of K lies between -1 and -3 eV for the long range interaction.

It may therefore be appropriate to assert that for the description of the early stage in a reaction between a ketone and a hydrogen donor the value of K lies in the range -1 to -3 eV while for the later stage of the same reaction the values of K lies in the range of -10 to -14 eV. Such approximations can only give a qualitative description of the reaction paths and also an order of magnitude for the interaction energy. The variations of the values of K within these two ranges do not, however, affect the trends of the results and hence the conclusions drawn from the results are not modified by such variations.

2.2. Energy level diagram

The energies of the various orbitals are obtained from the combination of photoelectron spectroscopic and UV spectral data. The lone pair ionization potentials of most carbonyl compounds are about 10 eV [22]. The energies of the highest occupied and the lowest unoccupied π orbitals of a ketone are obtained from the experimental values of the π ionization potential and of the lowest triplet $\pi\pi^*$ transition energy. The relative positions of the remaining π orbitals of a ketone such as acetophenone are obtained from Hückel calculations employing a spectroscopic value of -2.4 eV for the Hückel resonance integral β [23]. The energies of the lone pair orbitals in biacetyl are estimated at 9.6 eV and 11.5 eV from the photoelectron spectra. The energy required to remove an electron from a C—C bond in compounds like methane and ethane is approximately 13 eV [22], while the singlet excitation of a C—C bond requires about 10 eV. We can now therefore consider the energy level diagram shown in Fig. 3 for the purpose of an illustrative calculation.

3. Results and discussion

Figure 4 shows the variations of the interaction energies with the orbital overlap S for the in-plane hydrogen abstraction process (i.e. the mechanism of Fig. 1) during the early and later stages of the reaction. The results show that the $n\pi^*$ state of a ketone should be most reactive while the reaction with its ground and $\pi\pi^*$ states are forbidden. The rising trend in the early stage of the reaction path of the $n\pi^*$ state shows the presence of a barrier. However, with the present method, neither the height of the barrier can be estimated nor can its origin be determined. A pure $n\pi^*$ triplet state such as that of valerophenone shows an activation energy of 5 kcal mol^{-1} for the type II process [24]. In contrast, if the reaction is to take place in a perpendicular plane (i.e. the mechanism of Fig. 2), hydrogen abstraction becomes forbidden for all three different electronic states of acetophenone (Fig. 5). The above results strongly suggest that ketones undergo the in-plane
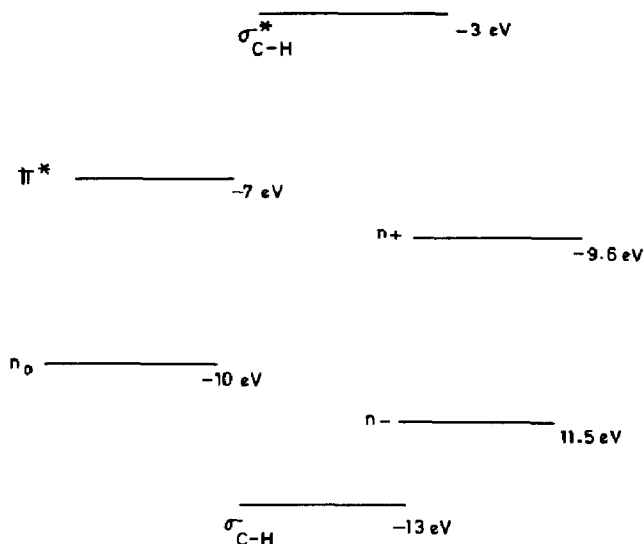
Fig. 3. Energy level diagram. The n_+ and n_- levels refer to the symmetric and antisymmetric combinations of the lone pair orbitals on the two oxygen atoms of biacetyl.

reaction with a hydrogen donor and regardless of the extent of their conjugation they abstract a hydrogen atom in their $n\pi^*$ state with an almost equal rate under similar conditions. The observed rate constant data which are shown in Table 1 for acetone, benzophenone and acetophenone with a common hydrogen donor confirm this finding.
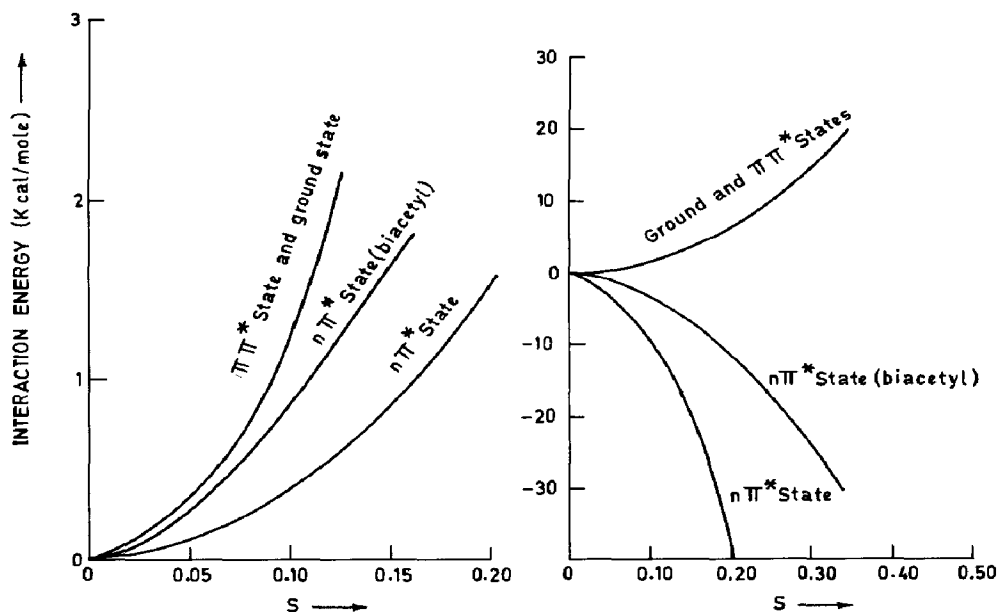

Fig. 4. Variations of the interaction energies (kcal mol^{-1}) of the various electronic states of ketones with the intermolecular orbital overlap S for (a) the early stage ($K = -3$ eV) and (b) the later stage ($K = -12$ eV) of the in-plane reaction.
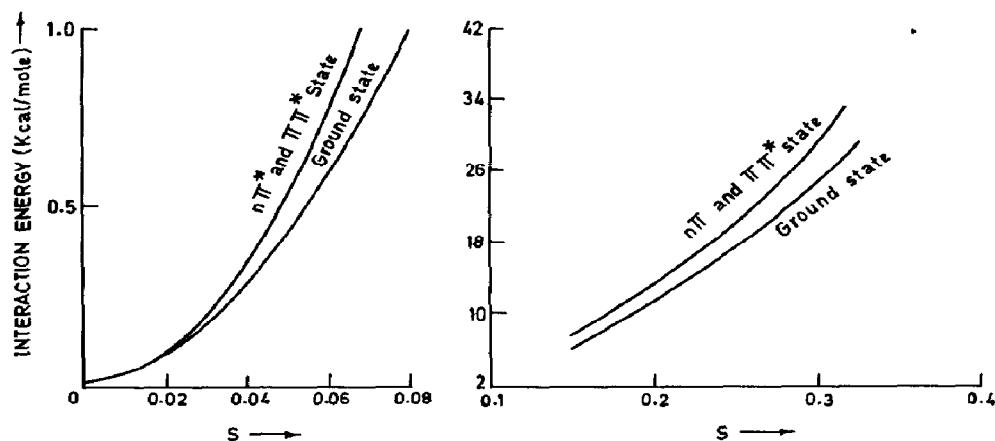
Fig. 5. Variations of the interaction energies (kcal mol^{-1}) of the various electronic states of acetophenone with the intermolecular orbital overlap S for (a) the early stage ($K = -3$ eV) and (b) the later stage ($K = -12$ eV) of the perpendicular plane reaction.

Biacetyl has a *trans*-planar configuration in its ground state [27]. The spectroscopic evidence also indicates that biacetyl emits from a coplanar conformation [28]. A *trans*-coplanar conformation in the triplet $n\pi^*$ state of biacetyl is also indicated from the photochemical behaviour of α-diketones toward intramolecular hydrogen abstraction [29]. Both calculations [30] and photoelectron spectral data [31] give a strong indication that the lone pair electrons in biacetyl are strongly delocalized. Employing the energy level diagram of Fig. 3 and assuming a symmetric and antisymmetric combination of two 2p orbitals on the oxygen atoms for the lone pair orbitals the total interaction energy between the lowest $n\pi^*$ state and a C—H bond for the in-plane reaction is plotted against the intermolecular orbital overlap S in Fig. 4. The results show that with biacetyl the reaction is weakly allowed during both the early and later stages in comparison with the reactivity of the $n\pi^*$ state of a monoketone. Since the shapes of the reaction profiles depend heavily on the choice of the parameter K, it will be of interest to examine such diagrams for other values of K. Figure 6 shows the results for $K =$

TABLE 1

Rate constant data for intermolecular hydrogen abstraction by ketones from isopropanol

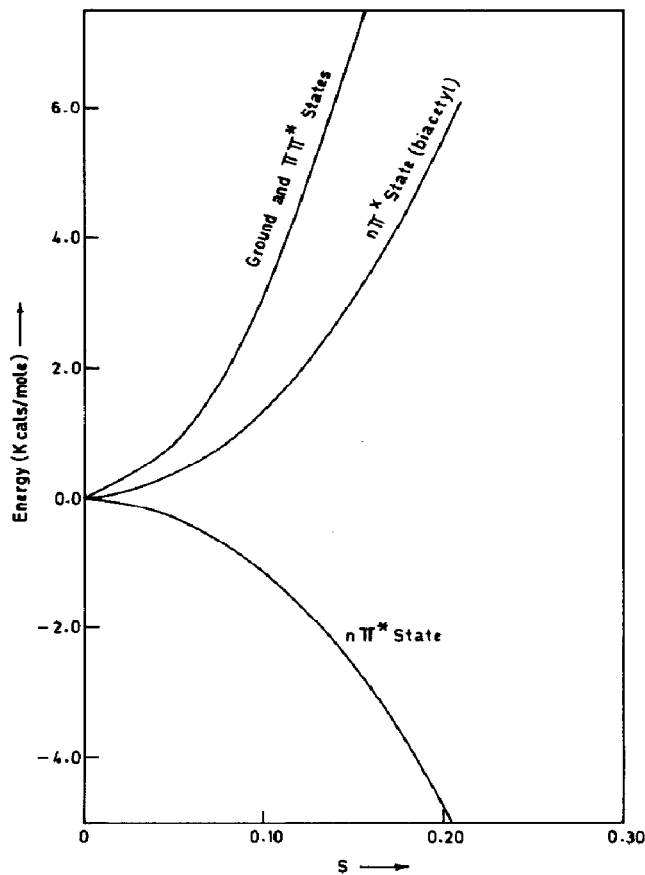| Ketone	Reactive state	K ($\times 10^{-6}$ s^{-1})	Reference
CH_3COCH_3	$^3n\pi^*$	1.00	25
$PhCOPh$	$^3n\pi^*$	1.00	26
$PhCOCH_3$	$^3n\pi^*$	1.00	26
p-$CH_3PhCOCH_3$	$^3\pi\pi^*$	0.1	8
$CH_3COCOCH_3$	$^3n\pi^*$	0.005	26

Fig. 6. Variation of the interaction energies (kcal mol^{-1}) of the various electronic states of ketones with S for $K = -6$ eV.

—6 eV. Once again, it reveals that the reaction rates for the in-plane process decrease in the order

$$n\pi^*(\text{monoketone}) > n\pi^*(\text{biacetyl}) > \pi\pi^* \text{ and ground states}$$

Thus our main conclusion is not affected by variation of the parameter K and is in general agreement with the observed rate constant data of Table 1. The results further reveal that the extensive delocalization of the lone pair electrons in biacetyl is responsible for the reduced reactivity of biacetyl in its $n\pi^*$ state.

When the conjugation of the π electrons is not extended beyond the carbonyl group, as in acetone and formaldehyde, the plots of the interaction energies of hydrogen abstraction *versus* orbital overlap shown in Fig. 7 for the perpendicular plane reaction reveal that reaction with the $\pi\pi^*$ state is allowed while those with the ground and $n\pi^*$ states are forbidden. Since for such ketones the lowest triplet $n\pi^*$ state lies only about 0.5 eV below the triplet $\pi\pi^*$ state, the two zero order reaction surfaces can cross. Since chemical reaction involves a displacement of the nuclei with concomitant
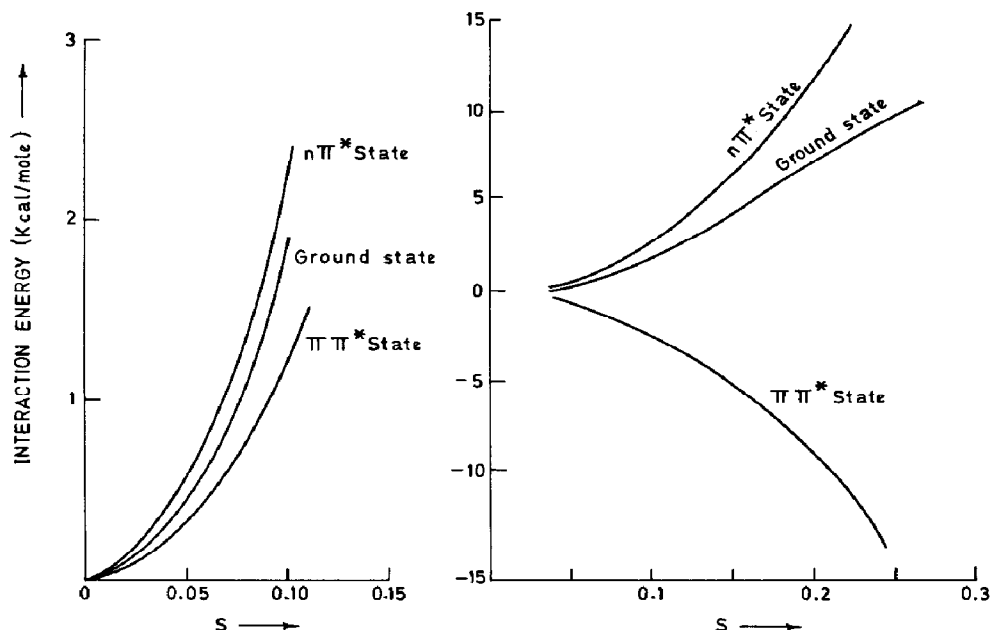
Fig. 7. Variations of the interaction energies of the various electronic states of acetone with the intermolecular orbital overlap S for (a) the early stage ($K = -3$ eV) and (b) the later stage ($K = -12$ eV) of the perpendicular plane reaction.

destruction of the symmetry plane of the reaction, a change in the hamiltonian can cause the mixing of the $\pi\pi^*$ state with the $n\pi^*$ state and the crossing becomes avoided at the point of the intended crossing. Figure 8 shows schematically the reaction surfaces for the in-plane and perpendicular plane reactions of the $n\pi^*$ and $\pi\pi^*$ states of acetone. If the initial slope of the reaction profiles is any guide, the activation energy for the perpendicular plane reaction is higher than that for the in-plane reaction.

The foregoing results also suggest that if the triplet $\pi\pi^*$ state of a large highly conjugated ketone lies below the triplet $n\pi^*$ state (e.g. p-methyl acetophenone) the two reaction surfaces can cross at a later stage during the in-plane hydrogen abstraction process (Fig. 9). Once again, considering the initial slope of the reaction profiles the reaction from the $\pi\pi^*$ state requires an activation energy higher than that required for the $n\pi^*$ state.

In order to examine whether deviation from perfect planarity affects the crossing of the reaction profiles, we imagine a plane containing the C—H bond of a hydrogen donor passing through the oxygen atom of the carbonyl group and making an angle α with the plane containing the carbonyl group of the ketone as shown in Fig. 10. For a given value of the intermolecular orbital overlap, say $S = 0.05$, the interaction energies for the hydrogen abstraction process are plotted against the angle α in Fig. 11 for the $\pi\pi^*$ and $n\pi^*$ states of acetophenone. Figure 11 reveals that, except when the reaction takes place in a perpendicular plane, the reaction profiles of the $n\pi^*$ and $\pi\pi^*$
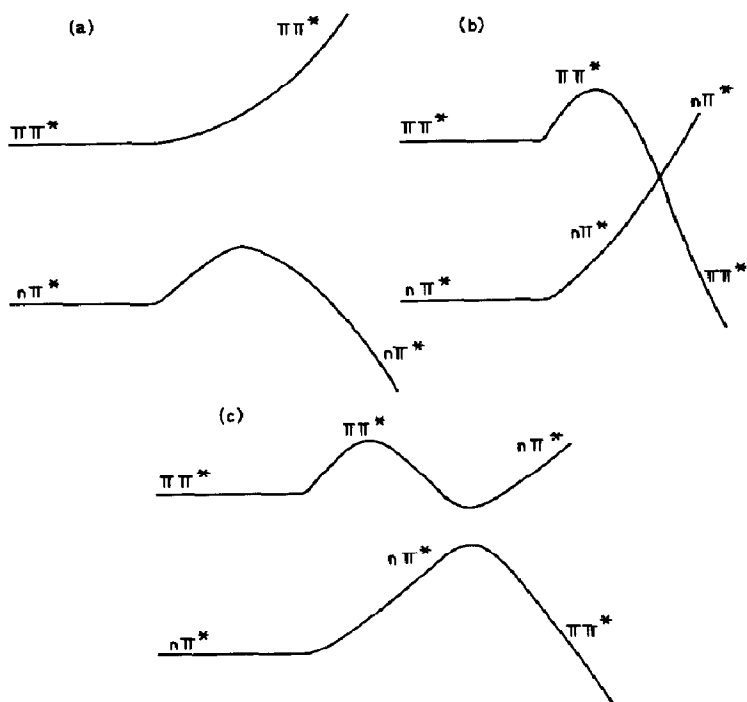
Fig. 8. The schematic reaction surfaces for (a) in-plane and (b), (c) perpendicular plane reactions of the $^3n\pi^*$ and $^3\pi\pi^*$ states of acetone; parts (b) and (c) refer respectively to the crossing and avoided crossing of the reaction profiles.

states are not parallel and hence the perfect coplanarity of the reaction plane is not a rigorous requirement for the crossing of the two reaction profiles.

In this context it will be appropriate to mention that two other mechanisms have been proposed to explain the reaction of the $\pi\pi^*$ state of a ketone. According to Wagner [32], in ketones where the energy gap between the $n\pi^*$ and $\pi\pi^*$ triplet states is only a few kcal mol^{-1} the mechanism of the reaction involves thermal excitation of the $\pi\pi^*$ state to the $n\pi^*$ state from which the reaction actually occurs. Yang [8, 9] has proposed that, since the $n\pi^*$ and $\pi\pi^*$ triplets mix vibronically in ketones, a small amount of $n\pi^*$ character mixed into the lowest $\pi\pi^*$ triplet gives that state $n\pi^*$ reactivity. The present analysis suggests that reaction from the triplet $\pi\pi^*$ state is
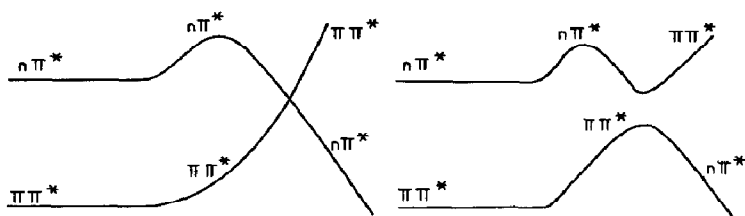
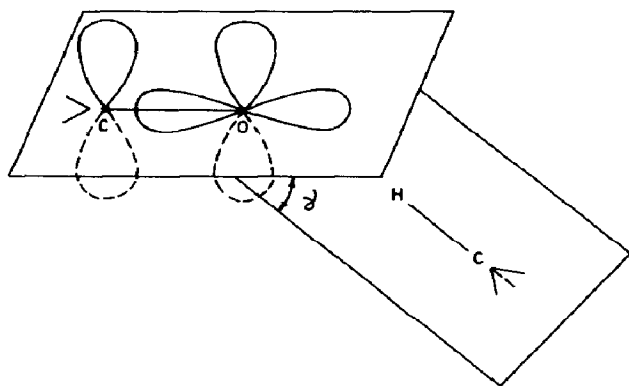Fig. 9. The crossing and the avoided crossing of the reaction profiles of p-methyl acetophenone.

Fig. 10. A plane containing the C—H bond makes an angle α with the plane of the carbonyl group.

possible owing to the crossing of the zero order reaction surfaces of the $n\pi^*$ and $\pi\pi^*$ states of the ketone.

Thus, Figs. 8 and 9 show that, in a one-electron description if necessary, an n electron of a ketone can change to a π electron at a later stage in a perpendicular plane process while a π electron changes to an n electron during the in-plane process. We therefore wish to assert that the behaviour of
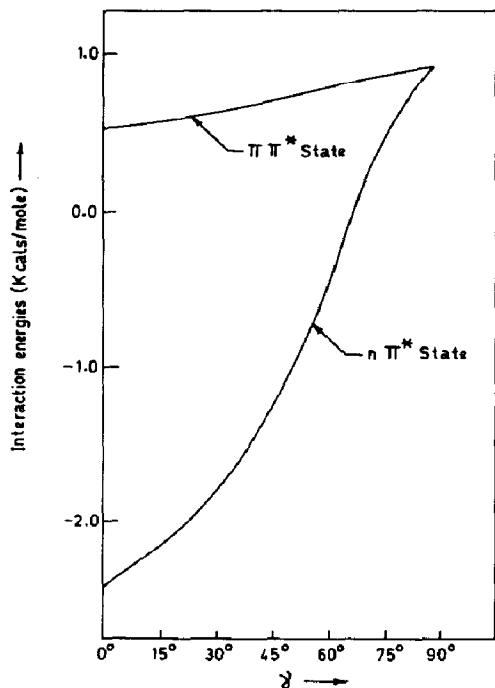

Fig. 11. Variations of the interaction energies (kcal mol^{-1}) of the $n\pi^*$ and $\pi\pi^*$ states of acetophenone with the dihedral angle α when the magnitude of the orbital overlap S is 0.05 and $K = -12$ eV.

a $2p_\pi$ orbital on the oxygen atom towards a hydrogen donor in a perpendicular plane process is identical to that of a $2p_\sigma$ (lone pair) orbital in an in-plane process. However, if an electron in a π orbital is highly delocalized, as in acetophenone, the availability of an electron on the oxygen nucleus in the perpendicular plane (Fig. 2) is low. In contrast, an electron in the oxygen lone pair orbital is localized on the oxygen atom in the plane of the molecule (Fig. 1); hence the in-plane reaction from the $n\pi^*$ state is allowed while the perpendicular plane reaction from the $\pi\pi^*$ state is forbidden. If conjugation is not extensive, as in acetone or formaldehyde, the perpendicular plane reaction from the $\pi\pi^*$ state is possible. Since for such ketones the $n\pi^*$ state is the lowest electronic state, hydrogen abstraction by the $\pi\pi^*$ state is not likely to be observable because the rate of hydrogen abstraction is slow compared with the internal conversion to the lowest $n\pi^*$ state.

4. Conclusions

The significant conclusions to be derived from our analysis are as follows.

(1) Ketones, preferentially undergo in-plane (Fig. 1) hydrogen abstraction and regardless of the extent of their conjugation with the carbonyl group they abstract a hydrogen atom in their triplet $n\pi^*$ state with an almost equal rate under similar conditions.

(2) If the conjugation of the $2p_\pi$ orbital on the oxygen atom in ketones is not extensive, abstraction can also take place in the perpendicular plane.

(3) Extensive delocalization of the lone pair electrons reduces the reactivity of the $n\pi^*$ state towards hydrogen abstraction.

(4) For large ketones where the energy of the triplet $\pi\pi^*$ state lies below that of the triplet $n\pi^*$ state, in-plane reaction of the $\pi\pi^*$ state takes place owing to the crossing of the zero order reaction profiles of the $n\pi^*$ and $\pi\pi^*$ states.

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