

## ORIGIN OF THE ACTIVATION BARRIER IN THE PROCESS OF HYDROGEN ABSTRACTION: THE PERTURBATION TREATMENT

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### Summary

The perturbation treatment previously given is extended to explain the process of hydrogen abstraction from the various hydrogen donor molecules by the triplet  $n\pi^*$  state of ketones or the ground state of the alkyl or alkoxy radical. The results suggest that, as the ionization energy of the donor bonds is decreased, the reaction is accelerated and it is not influenced by the bond strength of the donor bonds. The activation barrier in such reactions arises from a weakening of the charge resonance term as the ionization energy of the donor bond increases.

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### 1. Introduction

In a previous publication [1] we have reported an estimate of the change in energy during hydrogen abstraction by ketones as a function of the reaction coordinate, employing perturbation theory. Our results suggest that ketones preferentially undergo in-plane reaction and abstract a hydrogen atom from a C—H bond in their triplet  $n\pi^*$  state. The observed activation energies for the various intermolecular and intramolecular hydrogen abstraction process by the  $n\pi^*$  excited ketones are usually in the range 3 - 7 kcal mol<sup>-1</sup> [2]. In contrast, the bond energies of the donor bonds in the hydrogen donor molecule are in the range 90 - 100 kcal mol<sup>-1</sup>. Although a qualitative correlation [2, 3] between the bond energies in a related series of molecules and the rate constants of the process of hydrogen abstraction is found, this is not of much relevance to the mechanism of the reaction, because the bond-breaking step of the donor bond cannot be the rate-determining step in such reactions. In fact, with unrelated molecules [4] there is no correlation between the rate constant and bond strength of the donor bonds. According to Heller [5], the rate-determining step in the photochemical hydrogen abstraction process is the transfer of energy from photo-excited ketones to the C—H stretching mode of the donor molecule. This could give rise to a large vibrational excitation of the local C—H vibra-

tions which would result in breakage of the C—H bond. Heller [5] further concluded that, the lower the bond energy, the higher is the photochemical reactivity. Although this model can explain the isotope effect in such reactions, this view was seriously questioned by Yip and Siebrand [4] who concluded that the energy transfer cannot be the rate-determining step and that Heller's model [5] which is based on intramolecular radiationless transitions is not applicable. A theoretical model for photochemical reactions based on an analogy with a radiationless transition but incorporating a rapid vibrational redistribution has been developed by Rice [6]. However, because of its complexity, no comparison with experiment is possible.

The electronic feature of the  $n\pi^*$  state of a carbonyl compound is similar to that of an alkoxy or an alkyl radical which has an odd electron in its non-bonding molecular orbital with considerable p character. These radicals in their ground state do not have excess energy to transfer, but many experiments [2, 3, 7, 8] reveal that the primary steps in the photochemical reactions of the  $n\pi^*$  state of ketones and the thermal reaction of the alkoxy or alkyl radicals are similar. This suggests that the reaction mechanisms of the excited ketones and the ground state of the alkoxy or alkyl radicals are likely to be the same. The observed isotope effect in the hydrogen abstraction reactions can be explained on the basis of absolute reaction rate theory and a three-mass point model of the activated complex [7].

In this paper we shall present an analysis based on the perturbation method to explain the process of hydrogen abstraction from the various hydrogen donors. Although the perturbation method does not attempt to calculate the activation energy, an attempt is made here, however, to understand the origin of the activation barrier during the early stage of this reaction and to prove that the activation energy does not influence the bond strength of the donor bonds. Our argument applies equally to hydrogen abstraction by radicals because of the similar electronic features of the radicals and the  $n\pi^*$  state of the carbonyl compounds.

## 2. Outline of the perturbation method

A detailed theory of the perturbation method has been discussed previously [1]. For the in-plane reaction between a carbonyl group and a C—H bond of the hydrogen donor, the relevant orbitals are the oxygen lone pair orbital  $n_0$  and the  $\sigma_0$  and  $\sigma_0^*$  orbitals of the C—H bond. The total change in energy during the in-plane reaction with the  $n\pi^*$  state of a ketone is given by [1]

$$\Delta E = \Delta E_{n_0}^{(2)} + 2\Delta E_{\sigma_0}^{(2)} \quad (1)$$

where

$$\Delta E_{n_0}^{(2)} = \frac{(\langle n_0 | H | \sigma_0 \rangle - S_{n_0\sigma_0} E_{n_0})^2}{E_{n_0} - E_{\sigma_0}} + \frac{(\langle n_0 | H | \sigma_0^* \rangle - S_{n_0\sigma_0^*} E_{n_0})^2}{E_{n_0} - E_{\sigma_0^*}} \quad (2)$$

$$\Delta E_{\sigma_0}^{(2)} = \frac{(\langle n_0 | H | \sigma_0 \rangle - S_{n_0 \sigma_0} E_{\sigma_0})^2}{E_{\sigma_0} - E_{n_0}} \quad (3)$$

where  $H$  is the total hamiltonian of the composite system,  $E$  the energy and  $S$  the overlap of the participating orbitals. The matrix elements  $\langle n_0 | H | \sigma_0 \rangle$  are given by [1]

$$\langle n_0 | H | \sigma_0 \rangle = \frac{1}{2} (E_{n_0} + E_{\sigma_0}) S_{n_0 \sigma_0} + \langle n_0 | V | \sigma_0 \rangle \quad (4)$$

$$\langle n_0 | V | \sigma_0 \rangle = K S_{n_0 \sigma_0} \quad (5)$$

The integral  $\langle n_0 | H | \sigma_0^* \rangle$  is defined analogously.

We assume that  $K = -4$  eV for the early stage and that  $K = -12$  eV for the later stage of the reaction. Such approximations can give only a qualitative description of the reaction path and have been discussed in a previous publication [1].

If  $E_{n_0}$  and  $E_{\sigma_0}$  happen to have the same value, *i.e.*  $E_{n_0} = E_{\sigma_0} = E_0$ , it is then necessary to solve the following determinant:

$$\begin{vmatrix} E_0 - E & \langle n_0 | H | \sigma_0 \rangle - S_{n_0 \sigma_0} E & 0 \\ \langle n_0 | H | \sigma_0 \rangle - S_{n_0 \sigma_0} E & E_0 - E & \langle n_0 | H | \sigma_0^* \rangle - S_{n_0 \sigma_0^*} E \\ 0 & \langle n_0 | H | \sigma_0^* \rangle - S_{n_0 \sigma_0^*} E & E_{\sigma_0^*} - E \end{vmatrix} = 0 \quad (6)$$

If  $E_1$ ,  $E_2$  and  $E_3$  are the three eigenvalues of eqn. (6) in the order of increasing energies, then

$$\Delta E = 2E_1 + E_2 - 3E_0 \quad (7)$$

The perturbed normalized  $\sigma$  and  $n$  orbitals are given by

$$|\sigma\rangle = (1 - \lambda^2)^{1/2} |\sigma_0\rangle + \lambda |n_0\rangle + \lambda' |\sigma_0^*\rangle \quad (8)$$

$$|n\rangle = (1 - \lambda_1^2 - \lambda_1'^2)^{1/2} |n_0\rangle + \lambda_1 |n_0\rangle + \lambda_1' |\sigma_0^*\rangle \quad (9)$$

where

$$\lambda = \frac{\langle \sigma_0 | H | n_0 \rangle - S_{n_0 \sigma_0} E_{\sigma_0}}{E_{\sigma_0} - E_{n_0}} \quad (10)$$

$$\lambda' = \frac{(\langle \sigma_0 | H | n_0 \rangle - S_{n_0 \sigma_0} E_{\sigma_0})(\langle n_0 | H | \sigma_0^* \rangle - S_{n_0 \sigma_0^*} E_{\sigma_0})}{(E_{\sigma_0} - E_{n_0})(E_{\sigma_0} - E_{\sigma_0^*})} \quad (11)$$

$$\lambda_1 = \frac{\langle n_0 | H | \sigma_0 \rangle - S_{n_0 \sigma_0} E_{n_0}}{E_{n_0} - E_{\sigma_0}} \quad (12)$$

$$\lambda_1' = \frac{\langle n_0 | H | \sigma_0^* \rangle - S_{n_0 \sigma_0^*} E_{n_0}}{E_{n_0} - E_{\sigma_0^*}} \quad (13)$$

It should be noted that  $\lambda'$  is proportional to the second power of the overlap while  $\lambda$ ,  $\lambda_1$  and  $\lambda_1'$  are proportional to the first power of the overlap.

Since we are dealing with the in-plane reaction of the  $n\pi^*$  state of a carbonyl compound and a  $\sigma$  bond of a hydrogen donor, the composite system contains effectively three electrons for the present purpose and dissociates into the  $(n_0)^1$  and  $(\sigma_0)^2$  configurations. The electron density difference  $\Delta\rho$  during the reaction can be defined as

$$\Delta\rho = 2\sigma^2 + n^2 - 2\sigma_0^2 - n_0^2 \quad (14)$$

Using eqns. (8) and (9) for the  $\sigma$  and  $n$  orbitals in eqn. (14),  $\rho$  can be split into terms of different orders in the overlap. Neglecting terms involving higher than the second order in the overlap, we may write

$$\Delta\rho = \Delta\rho^{(1)} + \Delta\rho^{(2)} \quad (15)$$

where

$$\Delta\rho^{(1)} = (4\lambda + 2\lambda_1)n_0\sigma_0 + 2\lambda_1'n_0\sigma_0^* \quad (16)$$

$$\Delta\rho^{(2)} = (\lambda_1^2 - 2\lambda^2)\sigma_0^2 + (2\lambda^2 - \lambda_1^2 - \lambda_1'^2)n_0^2 + \lambda_1'^2\sigma_0^{*2} + (4\lambda' + 2\lambda_1\lambda_1')\sigma_0\sigma_0^* \quad (17)$$

These equations show that the density change in the intermolecular region, *i.e.* in the region between the oxygen atom of the carbonyl and the hydrogen atom of the hydrogen donor, is proportional to the first power of the overlap while the density changes in the reactant molecules during the reaction are proportional to the second power of the overlap. It should be noted that, in thermal reactions involving closed-shell molecules,  $\Delta\rho^{(2)}$  is important. This has been emphasized by several researchers [9, 10] in determining the role of polarization in chemical reactions. In photochemical reactions or in thermal reactions involving radicals, we find that  $\Delta\rho^{(1)}$  is more important than  $\Delta\rho^{(2)}$ . Therefore, we concentrate on the change in  $\Delta\rho^{(1)}$  in the intermolecular O...H region. The lone pair orbital  $n_0$  is primarily an O 2p orbital  $\phi_O$  and, on the assumption that the carbon and hydrogen atoms have nearly the same electronegativity, the  $\sigma_0$  and  $\sigma_0^*$  orbitals are approximately given by

$$\begin{aligned} \sigma_0 &= \frac{1}{2^{1/2}} (\phi_H + \phi_C) \\ \sigma_0^* &= \frac{1}{2^{1/2}} (\phi_H - \phi_C) \end{aligned} \quad (18)$$

We may now write

$$\Delta\rho^{(1)} = \gamma\phi_H\phi_O \quad (19)$$

where

$$\gamma = \frac{1}{2^{1/2}} (4\lambda + 2\lambda_1 + 2\lambda_1') \quad (20)$$

and is proportional to the overlap  $S$ . The sign of  $\gamma$  determines the manner in which the electron distributions in the intermolecular O...H region change as the reaction proceeds. It should be noted that the sign of  $\gamma$  is not dependent on the assumption in eqn. (18) as long as the effect of the  $\sigma_0^*$  orbital is very small.

### 3. Energy level diagram

The lone pair ionization potentials of most carbonyl compounds are around 10 eV [11]. The ionization energies of the donor bond in the hydrogen donor molecules vary. The ionization energy of a C—H bond in compounds such as methane and ethane is approximately 13 eV [11]. The energy of the  $\sigma_0^*$  orbital is assumed to be  $-3$  eV [1]. The energies of the  $\sigma_0^*$  orbital of most hydrogen donor molecules are usually much higher than this according to both complete neglect of differential overlap (CNDO) and extended Huckel calculations. The effect of the  $\sigma_0^*$  orbital on  $\Delta E$  is therefore not serious. We mainly concentrate on the variation in the total interaction energy  $\Delta E$  with the position of the  $\sigma_0$  level relative to that of the  $n_0$  level in the energy level diagram of Fig. 1. We define  $\delta E$  as the difference between  $E_{n_0}$  which is always assumed to be  $-10$  eV and  $E_{\sigma_0}$  which depends on the hydrogen donor molecule.

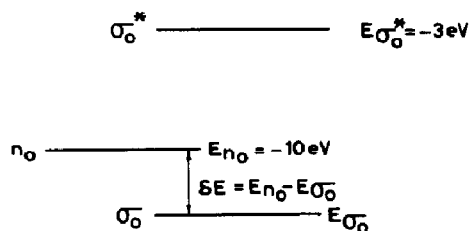


Fig. 1. Energy level diagram.

## 4. Results and discussion

### 4.1. Changes in energy and density during the reaction

Figure 2 shows the variation in the total interaction energies  $\Delta E$  with the orbital overlap  $S$  for the different values of  $\delta E$  during the early and later stages of the hydrogen abstraction process. Since the chemical non-crossing rule is assumed to be valid, the activation energy differences are given by differences in the initial slopes of the reaction profiles [12]. Figure 2 shows that, as  $\delta E$  increases, the activation energy for the reaction increases. When  $\delta E = 0$ , there is no activation barrier for the reaction. This is in qualitative agreement with the fact that the formation of  $\text{He}_2^+$  in the  $^2\Sigma_u$  state from the helium atom and the  $\text{He}^+$  ion does not require any activation energy.

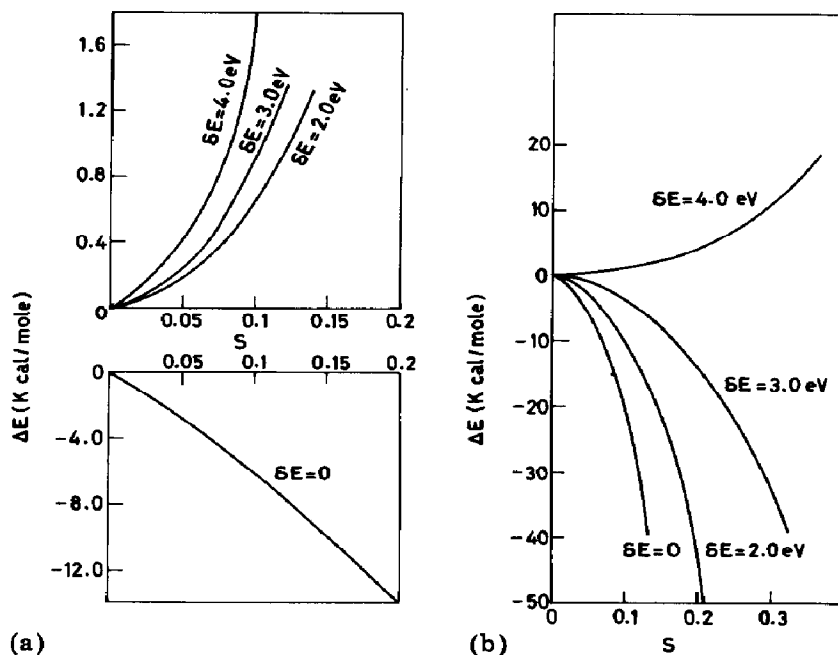
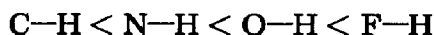


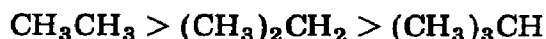
Fig. 2. Variations in the interaction energies with the intermolecular overlap  $S$  for (a) the early stage ( $K = -4$  eV) and (b) the later stage ( $K = -12$  eV) of the in-plane reaction.

Both the Hartree-Fock calculations and the experimental determination of ionization energies of the C-H, N-H, O-H and F-H bonds in simple molecules [13, 14] reveal that the ionization energies increase in the order



The results in Fig. 2 now suggest that the difficulty of abstracting the hydrogen atom from the different donor bonds by the  $n\pi^*$  state of a ketone increases in the same order as above. This is in agreement with the fact that the  $n\pi^*$  state of a ketone rarely abstracts the hydrogen atom from the O-H or F-H bonds in simple molecules.

The extended Hückel calculations [15] on complex alkanes reveal that the ionization potentials and the positive charge localized on the hydrogen atom in the primary, secondary and tertiary C-H bonds decrease in the order



Accordingly the activation energy for the hydrogen abstraction process should decrease in the same order. In quantitative agreement with this result, it is found (Table 1) that, as the hydrogen atom being abstracted from the  $\gamma$  C atom in a type II elimination process is varied from a primary to a tertiary hydrogen, a marked increase in the rate constants of the reaction is observed. Since the hydrogen abstraction by alkyl radicals operates by a

TABLE 1

Relative rate constants for the type II elimination process and for the hydrogen abstraction by the methyl radical from primary, secondary and tertiary aliphatic hydrocarbons

Molecule	Relative [16] rate constant	Molecule	Relative [8] rate constant
PhCOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -H	1.0	R-CH <sub>2</sub> -H	1.0
PhCOCH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )-H	17.6	R <sub>2</sub> -CH-H	4.3
PhCOCH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> -H	75.8	R <sub>3</sub> -C-H	46.0

similar mechanism, the relative rates of hydrogen abstraction from primary, secondary and tertiary C-H bonds by a methyl radical are shown in Table 1 and these are also in qualitative agreement with our prediction.

Figure 3 shows the variation in  $\gamma$  with the orbital overlap  $S$  for different values of  $\delta E$  during the early and later stages of this reaction. The negative values of  $\gamma$  for large values of  $\delta E$  during the early stages of the reaction are consistent with the presence of a large activation barrier. In contrast, the increasing positive values of  $\gamma$  during the later stages of the reaction create favourable conditions for the formation of the chemical bond -O-H between the oxygen atom of the carbonyl and the hydrogen atom of the hydrogen donor.

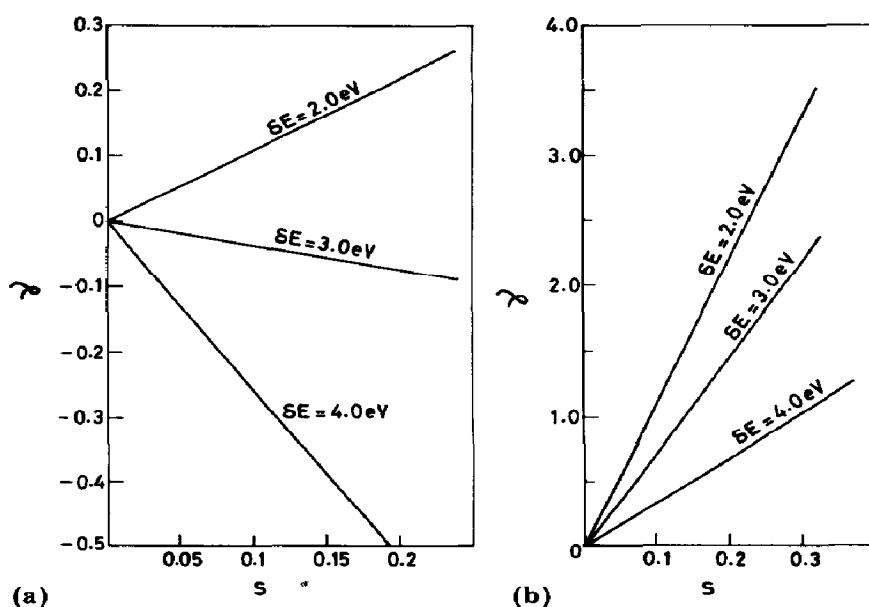


Fig. 3. Variations in  $\gamma$  with the intermolecular overlap  $S$  for (a) the early stage ( $K = -4$  eV) and (b) the later stage ( $K = -12$  eV) of the in-plane reaction.

#### 4.2. Origin of the activation barrier

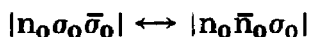
We shall now address ourselves to the question of the origin of the activation barrier for  $\delta E > 0$  in such reactions. In order to understand qualitatively the origin of the activation barrier, we ignore the effect of the  $\sigma_0^*$  orbital on the total interaction energy  $\Delta E$ . We then have, for  $\delta E = 0$ ,

$$\Delta E = -3\langle n_0 | V | \sigma_0 \rangle S + \langle n_0 | V | \sigma_0 \rangle \quad (21)$$

and, for  $\delta E > 0$ ,

$$\begin{aligned} \Delta E = \frac{1}{\delta E} \{ S^2 (E_{n_0}^2 + E_{\sigma_0}^2) + S E_{\sigma_0} (E_{n_0} S + 2\langle n_0 | V | \sigma_0 \rangle) \} - \\ - 2\langle n_0 | V | \sigma_0 \rangle S - \frac{\langle n_0 | H | \sigma_0 \rangle^2}{\delta E} \end{aligned} \quad (22)$$

These equations are obtained in a very straightforward manner and eqn. (4) is substituted for the integral  $\langle n_0 | H | \sigma_0 \rangle$ . The first term of eqn. (21) and the first two terms of eqn. (22) are repulsive because the integral  $\langle n_0 | V | \sigma_0 \rangle$  and the energies  $E_{n_0}$  and  $E_{\sigma_0}$  are negative. This repulsion arises primarily from the exchange of electrons between the  $n_0$  and  $\sigma_0$  orbitals of the reactants. The second term in eqn. (21) is the attractive charge resonance term which arises from resonance between the two electron configurations



of the same energy. Since this term dominates in eqn. (21) for all values of  $S$ ,  $\Delta E$  always decreases and there is no barrier for the reaction. For  $\delta E > 0$ , the attractive charge resonance term is given by the third term of eqn. (22) which shows that, as  $\delta E$  increases, the magnitude of this resonance term decreases. This seems to suggest very strongly that the activation barrier during the early stages arises from the decreasing importance of the charge resonance term as  $\delta E$  increases. During the later stage of this reaction, the integral  $\langle n_0 | H | \sigma_0 \rangle$  is very large and the attractive charge resonance term may dominate in eqn. (22) when the reaction path is downhill.

## 5. Conclusions

We may now conclude that the in-plane hydrogen abstraction process by the  $n\pi^*$  state of a ketone or the ground state of an alkyl radical is understood primarily by the interaction of the non-bonding orbital of the odd electron and the  $\sigma_0$  orbital of the donor bond. This reaction is accelerated as the ionization energy of the donor bond decreases. The activation barrier for the lower donor ability of the donor bond arises from a weakening of the charge resonance term.



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