

## PHOTOCHEMICAL HYDROGEN ABSTRACTION AS A RADIATION-LESS TRANSITION IN THE PHOTOKETONIZATION OF $\beta$ -DI-CARBONYL COMPOUNDS

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### Summary

The photoketonization of two series of  $\beta$ -dicarbonyl compounds was treated in terms of the tunnel effect theory as a radiationless transition. The first series involves derivatives of the ethyl ester of benzoylacetic acid and the second series comprises derivatives of acetoacetic acid. These series showed a strong dependence of the overall photoketonization reaction rate constants on the reaction coordinate, which is constant for a given series. The rate constants of the second series were reproduced using a single value of the enol OH bond energy  $D_{OH}$ , whereas the rate constants  $k_r$  of the first series show a marked dependence on  $D_{OH}$  and a correlation between  $\log k_r$  and  $D_{OH}$  was found. The successful application of the tunnel effect theory to the photoketonization processes of the compounds studied was interpreted to imply that these processes may in fact involve through-space photochemical hydrogen migration which is governed by the tunnel effect.

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### 1. Introduction

Data on the photoketonization kinetics in solutions of  $\beta$ -dicarbonyl compounds [1, 2] have shown that this process can be considered as an intramolecular photoinitiated hydrogen migration. However, using the orbital symmetry conservation rules, it has been concluded [3] that the hydrogen migration most probably takes place through the reaction space defined by the bond to be broken and the bond to be formed, and not through the chemical bonds located between the reaction sites. Consequently, the photoinitiated prototropic conversion may be regarded as an intramolecular radiationless process. Such a conversion may be described at least in principle on the basis of general theoretical considerations (see for instance ref. 4). Such considerations may be used to find the relations between the structural peculiarities of the molecules studied and their ability to

TABLE 1

Derivatives of the ethyl ester  
of benzoylacetic acid  
(G—C<sub>6</sub>H<sub>4</sub>—CO—CH<sub>2</sub>—COOC<sub>2</sub>H<sub>5</sub>)

| Compound | G                           |
|----------|-----------------------------|
| 1        | H                           |
| 2        | <i>p</i> -CH <sub>3</sub>   |
| 3        | <i>m</i> -CH <sub>3</sub>   |
| 4        | <i>o</i> -CH <sub>3</sub>   |
| 5        | <i>p</i> -NO <sub>2</sub>   |
| 6        | <i>m</i> -NO <sub>2</sub>   |
| 7        | <i>m</i> -CH <sub>3</sub> O |
| 8        | <i>p</i> -Cl                |
| 9        | <i>p</i> -Br                |

TABLE 2

Derivatives of acetoacetic acid (R<sub>1</sub>—CO—C(R<sub>2</sub>)H—COOR<sub>3</sub>)

| Compound | R <sub>1</sub>                                    | R <sub>2</sub>                                | R <sub>3</sub>  |
|----------|---|---|---|
| 10       | CH <sub>3</sub> CH <sub>2</sub>                   | H   | C <sub>2</sub> H <sub>5</sub>                                   |
| 11       | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub>   | H   | C <sub>2</sub> H <sub>5</sub>                                   |
| 12       | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>   | H   | C <sub>2</sub> H <sub>5</sub>                                   |
| 13       | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub>   | H   | C <sub>2</sub> H <sub>5</sub>                                   |
| 14       | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub>   | H   | C <sub>2</sub> H <sub>5</sub>                                   |
| 15       | (CH <sub>3</sub> ) <sub>2</sub> CH                | H   | C <sub>2</sub> H <sub>5</sub>                                   |
| 16       | (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> | H   | C <sub>2</sub> H <sub>5</sub>                                   |
| 17       | C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>     | H   | C <sub>2</sub> H <sub>5</sub>                                   |
| 18       | CH <sub>3</sub>                                   | CH <sub>3</sub>                               | C <sub>2</sub> H <sub>5</sub>                                   |
| 19       | CH <sub>3</sub>                                   | CH <sub>3</sub> CH <sub>2</sub>               | C <sub>2</sub> H <sub>5</sub>                                   |
| 20       | CH <sub>3</sub>                                   | C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> | C <sub>2</sub> H <sub>5</sub>                                   |
| 21       | CH <sub>3</sub>                                   | CH(CH <sub>3</sub> ) <sub>2</sub>             | C <sub>2</sub> H <sub>5</sub>                                   |
| 22       | CH <sub>3</sub>                                   | H   | CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>             |
| 23       | CH <sub>3</sub>                                   | H   | C <sub>5</sub> H <sub>11</sub>                                  |
| 24       | CH <sub>3</sub>                                   | H   | CH <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub> |
| 25       | CH <sub>3</sub>                                   | H   | CH <sub>2</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub> |
| 26       | CH <sub>3</sub>                                   | H   | C <sub>6</sub> H <sub>11</sub>                                  |
| 27       | CH <sub>2</sub>                                   | H   | CH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub>              |
| 28       | CH <sub>3</sub>                                   | H   | H <sub>2</sub> C—◇  |
| 29       | CH <sub>3</sub>                                   | H   | H <sub>2</sub> C—C <sub>6</sub> H <sub>5</sub>                  |

undergo a type of photoinitiated transformation, *i.e.* they may throw light on the mechanism of the process under consideration. However, the complex nature of this orthodox approach, as well as the necessity to introduce physical and mathematical approximations related to the application of the theory, reduces the efficiency of this method considerably.

An approach using the tunnel theory for radiationless processes has recently been developed [5]. This approach is thought to be free of the aforementioned disadvantages. Results have also been obtained (see for in-

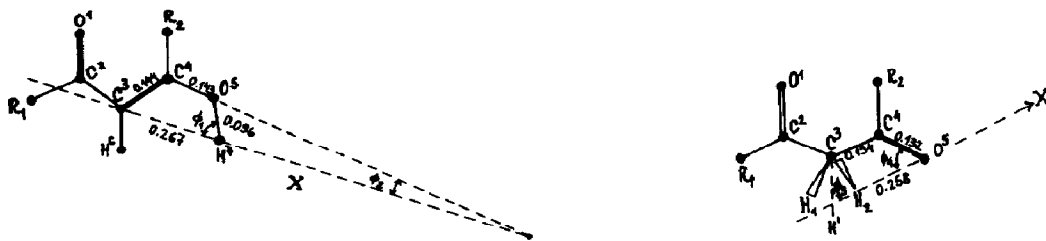


Fig. 1. Assumed (C(3)=C(4), C(4)—O(5), O(5)—H(7)) and calculated (C(3)—H(7)) bond distances in the unchelated sickle form of the enols. Both carbon and oxygen are assumed to be  $sp^2$  hybridized. Calculated:  $\phi_1 = 68.84^\circ$ ,  $\phi_2 = 8.84^\circ$ .  $X$  denotes the reaction coordinate.

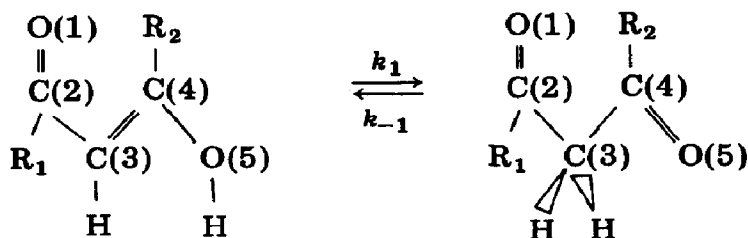
Fig. 2. Assumed (C(3)—C(4), C(4)=O(5), C(3)—H') and calculated (O(5)—H') distances in the keto form. C(2), C(4) and O(5) are assumed to be  $sp^2$  hybridized and C(3) is assumed to be  $sp^3$  hybridized. H(1) and H(2) are above and below the molecular plane and H' is their projection on this plane.  $\phi_3 = 66.56^\circ$ ,  $\phi_4 = 47.55^\circ$ .  $X$  is the reaction coordinate.

stance refs. 6 and 7) which demonstrate the applicability of this approach to photochemical conversions which are similar in nature to those considered in the present work.

We report here an attempt to discuss the photoketonization process of  $\beta$ -dicarbonyl compounds in terms of the tunnel effect theory of radiationless transitions.

### 1.1. Objects, geometrical model and reaction coordinates

The two series of  $\beta$ -dicarbonyl compounds given in Tables 1 and 2 were studied in this work. Figures 1 and 2 show geometrical models for the two tautomeric forms. The bond lengths for these models were taken from standard reference sources [8]. It can be seen from these figures that photo-initiated hydrogen transfer presupposes the formation of a transition state with the shape of a distorted trapezium. Figures 1 and 2 were drawn using the assumption that the sickle form [9, 10], *i.e.* the *trans*-unchelated rotamer, of the enol is the precursor of the keto form in the course of the photoinitiated conversion:



The reaction coordinate was taken along the direction between the OH hydrogen and C(3), in accordance with the through-space mechanism thought to be operative in the case under consideration [3].

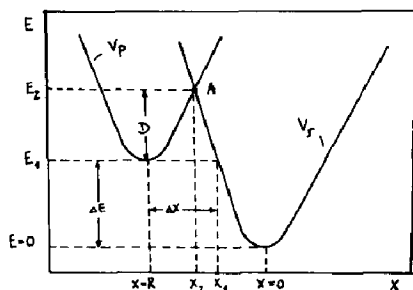


Fig. 3. Illustration of the quantities involved in the description of the crossing of the two potential energy curves:  $V_p$ , for the products;  $V_r$ , for the reactants;  $X$ , the reaction coordinate;  $R$ , the displacement of the two parabolas.

### 1.2. Computational procedure

This procedure has been described in detail elsewhere [6, 11]. Since the graphical solution admits certain inaccuracy, we solved the problem analytically using a computer program. This program was based on the following equation:

$$k_r = k_0 \exp \left\{ -\frac{1}{\hbar} (2\mu D)^{1/2} \Delta X \right\} \quad (1)$$

The quantities featuring in expression (1) are illustrated in Fig. 3. The reduced mass  $\mu$  of the OH and CH oscillators is defined as

$$\mu^{1/2} = \mu_{OH}^{1/2} + \mu_{CH}^{1/2} \quad (2)$$

For intramolecular processes the transmission factor  $k_0$  is taken to be  $10^{13} \text{ s}^{-1}$ .

By definition the two potential energy curves are

$$V_r = \frac{1}{2} f_r X^2$$

and (3)

$$V_p = \Delta E + \frac{1}{2} f_p (X - R)^2$$

where the subscripts r and p refer to reactants and products respectively and  $f$  denotes the force constant giving the curvature of the potential energy curve.

The change in energy taking place on conversion of one tautomeric form into the other is

$$\Delta E = E_{e1} + D_1 - D_2 \quad (4)$$

where  $E_{e1}$  is the electronic excitation energy (equated in our case to the energy of the first singlet-singlet transition observed in the spectra of the enol forms of the compounds),  $D_1$  is the energy of the bond to be formed

(CH) and  $D_2$  is the energy of the bond to be ruptured (OH) during the reaction course.

At the point of intersection of the two potential energy curves (Fig. 3) we have

$$V_r(X_2) = V_p(X_2) \quad (5)$$

Substitution of eqns. (3) and (4) into eqn. (5) and rearrangement yields

$$X_2^2 + bX_2 + c = 0 \quad (6)$$

where

$$b = \frac{2f_p R}{f_r - f_p}$$

and

$$c = - \frac{2\Delta E + f_p R^2}{f_r - f_p} \quad (7)$$

If  $f_r > f_p$ , as is usually the case, the positive root of the quadratic eqn. (6) is

$$\begin{aligned} X_2 &= -\frac{b}{2} + \frac{1}{2}(b^2 - 4c)^{1/2} \\ &= \frac{R[\{2\Delta E(f_r - f_p) + f_r f_p\}^{1/2} - f_r]}{f_r - f_p} \end{aligned} \quad (8)$$

Since by definition (see Fig. 3)

$$E_2 = V_r(X_2) \quad (9)$$

using  $\Delta E = E_1$  we find

$$D = E_2 - E_1 = E_2 - \Delta E \quad (10)$$

To find  $\Delta X$ , we seek  $X_1$  from the condition

$$V_r(X_1) = \Delta E = \frac{1}{2} f_r X_1^2 \quad (11)$$

or

$$X_1 = (2\Delta E/f_r)^{1/2} \quad (12)$$

Then

$$\Delta X = R - X_1 = R - (2\Delta E/f_r)^{1/2} \quad (13)$$

Taking into consideration eqns. (2), (10) and (13) we can find the theoretical values of the rate constants from eqn. (1) if  $f_r$ ,  $f_p$ ,  $R$ ,  $E_{e1}$ ,  $D_1$  and  $D_2$  are known (or if  $D_1$ ,  $D_2$  and  $R$  are known for given experimental values of  $k_r$ ,  $f_r$ ,  $f_p$  and  $E_{e1}$ ).

To find  $k_r$  we have to calculate  $f_r$  and  $f_p$ . These are force constants defined with respect to the reaction coordinates and not with respect to the

TABLE 3

Force constants [9] for the bonds in the enol and keto forms of the  $\beta$ -dicarbonyl compounds studied

| Bond | $f^s (\times 10^7 \text{ cm}^{-1} \text{ nm}^{-2})$ | $f^b (\times 10^7 \text{ cm}^{-1} \text{ nm}^{-2})$ |
|------|---|---|
| C-H  | 2.52  | 0.3   |
| O-H  | 3.52  | 0.51  |
| C-O  | 2.52  | 0.3 <sup>a</sup>                                    |
| C=O  | 3.65  | 0.5 <sup>a</sup>                                    |

<sup>a</sup>Estimated values.

internal coordinates of the molecule. The two sets of force constants, defined with respect to the two sets of coordinates, may not be coincident and for this reason  $f_x$  and  $f_p$  have to be calculated from  $f^s$  and  $f^b$  and their projection on the reaction coordinate, namely

$$f_{xy} = f^s \cos \phi_i + f^b \sin \phi_i \quad (14)$$

where  $x$  and  $y$  denote the two reaction sites and  $s$  and  $b$  designate the stretching and bending modes of the bonds taking part in the conversion. The numerical values of  $f^s$  and  $f^b$  used in this work were taken from ref. 9 and are collected in Table 3. Thus

$$\begin{aligned} f_x^2 &= f_{\text{C-O}}^2 + f_{\text{OH}}^2 + 2f_{\text{C-O}}f_{\text{OH}} \cos \theta(\text{C-O}, \text{CH}) \\ f_x &= 3.30 \times 10^7 \text{ cm}^{-1} \text{ nm}^{-2} \end{aligned} \quad (15)$$

and

$$\begin{aligned} f_p^2 &= f_{\text{C=O}}^2 + f_{\text{CH}}^2 - 2f_{\text{C=O}}f_{\text{CH}} \cos \theta(\text{C=O}, \text{OH}) \\ f_p &= 2.96 \times 10^7 \text{ cm}^{-1} \text{ nm}^{-2} \end{aligned} \quad (16)$$

$f_{\text{C-O}}$ ,  $f_{\text{C=O}}$ ,  $f_{\text{OH}}$  and  $f_{\text{CH}}$  were calculated using eqn. (14) and the data collected in Table 3.

The sign in front of the third term for  $f_x$  is positive since the CO and OH oscillators have to change in phase; for  $f_p$  it is negative since, after the migration of the hydrogen atom, the oscillators CO and OH should vibrate in opposite phases.

The distance  $R$  (Fig. 3) was found from the expression

$$R^2 = r_{\text{OH}}^2 + r_{\text{CH}}^2 - 2r_{\text{OH}}r_{\text{CH}} \cos \theta(\text{OH}, \text{CH}) \quad (17)$$

where  $r = \Delta d$  is the change in length of the bond denoted in the subscript. On comparison of the two geometrical models given in Figs. 1 and 2, we find  $r_{\text{OH}} = 0.177 \text{ nm}$ ,  $r_{\text{CH}} = 0.155 \text{ nm}$  and  $r_{\text{CO}} = 0.021 \text{ nm}$ ; hence  $R = 0.075 \text{ nm}$ , a value which is rather close to that used in ref. 6 for the intramolecular hydrogen transfer reactions of ketones ( $R = 0.074 \text{ nm}$ ). The values of  $\cos \theta$  were calculated from the formula [6]

TABLE 4

Spectral, kinetic and photochemical data for compounds 1 - 9 in heptane solution ( $1 \times 10^{-4}$  mol l $^{-1}$ )

| Compound | $\tilde{\nu}$ (cm $^{-1}$ ) | $\epsilon$ (l mol $^{-1}$ cm $^{-1}$ ) | $f$  | $\tau \times 10^9$ (s) | $\log k_r$         | $\phi$ |
|----------|-----------------------------|--|------|------------------------|--------------------|--------|
| 1        | 34 480                      | 21 400                                 | 0.49 | 2.59                   | $-3.28 \pm 0.01$   | 0.53   |
| 2        | 34 010                      | 27 800                                 | 0.69 | 2.04                   | $-3.107 \pm 0.002$ | 0.73   |
| 3        | 34 480                      | 24 300                                 | 0.49 | 2.59                   | $-3.24 \pm 0.04$   | 0.60   |
| 4        | 35 200                      | 12 000                                 | 0.28 | 4.35                   | $-4.41 \pm 0.02$   | —      |
| 5        | 31 950                      | 27 800                                 | 0.60 | 2.47                   | $-3.18 \pm 0.02$   | 0.60   |
| 6        | 34 480                      | 23 800                                 | 0.53 | 2.40                   | $-3.44 \pm 0.01$   | 0.39   |
| 7        | 34 960                      | 23 400                                 | 0.52 | 2.38                   | $-3.20 \pm 0.03$   | 0.64   |
| 8        | 34 130                      | 24 200                                 | 0.54 | 2.40                   | $-3.10 \pm 0.01$   | 0.85   |
| 9        | 34 010                      | 27 600                                 | 0.61 | 2.14                   | $-3.010 \pm 0.005$ | 0.91   |

$\nu$ ,  $\epsilon$ ,  $f$  are the wavenumbers, extinction coefficients and oscillator forces respectively for the enol forms.  $\tau$  is the lifetime of the first excited singlet,  $k_r$  is the first-order reaction rate constant (s $^{-1}$ ) and  $\phi$  is the quantum yield.

TABLE 5

Spectral, kinetic and photochemical data for compounds 10 - 29 in heptane solution ( $1 \times 10^{-4}$  mol l $^{-1}$ )

| Compound | $\tilde{\nu}$ (cm $^{-1}$ ) | $\epsilon$ (l mol $^{-1}$ cm $^{-1}$ ) | $f$   | $\tau \times 10^9$ (s) | $\log k_r$       | $\phi$ |
|----------|-----------------------------|--|-------|------------------------|------------------|--------|
| 10       | 40 500                      | 16 300                                 | 0.429 | 2.15                   | $-3.79 \pm 0.17$ | 0.18   |
| 11       | 40 500                      | 17 000                                 | 0.470 | 1.96                   | $-3.69 \pm 0.12$ | 0.19   |
| 12       | 40 300                      | 17 400                                 | 0.474 | 1.96                   | $-3.64 \pm 0.11$ | 0.14   |
| 13       | 40 300                      | 14 800                                 | 0.383 | 2.43                   | $-3.49 \pm 0.07$ | 0.20   |
| 14       | 40 300                      | 12 400                                 | 0.343 | 2.71                   | $-3.69 \pm 0.14$ | 0.22   |
| 15       | 40 700                      | 17 000                                 | 0.441 | 2.07                   | $-3.64 \pm 0.14$ | 0.17   |
| 16       | 40 500                      | 17 400                                 | 0.451 | 2.04                   | $-3.60 \pm 0.20$ | 0.15   |
| 17       | 37 310                      | —                                      | —     | —                      | —                | —      |
| 18       | 38 910                      | 11 300                                 | 0.441 | 2.26                   | $-3.49$          | —      |
| 19       | 39 680                      | 11 000                                 | 0.285 | 3.37                   | $-3.85$          | —      |
| 20       | 38 460                      | 11 000                                 | 0.285 | 3.58                   | $-3.83$          | —      |
| 21       | 40 820                      | 11 100                                 | 0.296 | 3.06                   | $-3.77$          | —      |
| 22       | 40 300                      | 15 700                                 | 0.413 | 2.25                   | $-3.72 \pm 0.08$ | 0.17   |
| 23       | 40 700                      | 16 500                                 | 0.413 | 2.21                   | $-3.62$          | 0.06   |
| 24       | 40 700                      | 13 300                                 | 0.357 | 2.44                   | $-3.63 \pm 0.07$ | 0.14   |
| 25       | 40 300                      | 12 600                                 | 0.360 | 2.58                   | $-3.54 \pm 0.06$ | 0.13   |
| 26       | 40 700                      | 16 200                                 | 0.449 | 2.04                   | $-3.57 \pm 0.10$ | 0.06   |
| 27       | 39 700                      | 29 700                                 | 0.847 | 1.13                   | $-3.75$          | 0.04   |
| 28       | 40 700                      | 13 000                                 | 0.331 | 2.76                   | $-3.59 \pm 0.14$ | 0.13   |
| 29       | 40 500                      | 14 600                                 | 0.384 | 2.40                   | $-3.53 \pm 0.07$ | 0.14   |

The notation is the same as that used in Table 4.

TABLE 6

Displacement coordinates  $R$  calculated from the experimental rate constants  $k_r$  listed in Tables 4 and 5

| Series A |          | Series B |          |          |          |
|----------|----------|----------|----------|----------|----------|
| Compound | $R$ (nm) | Compound | $R$ (nm) | Compound | $R$ (nm) |
| 1        | 0.0808   | 10       | 0.0852   | 20       | 0.0853   |
| 2        | 0.0802   | 11       | 0.0850   | 21       | 0.0850   |
| 3        | 0.0807   | 12       | 0.0849   | 22       | 0.0851   |
| 4        | 0.0826   | 13       | 0.0847   | 23       | 0.0851   |
| 5        | 0.0789   | 14       | 0.0849   | 24       | 0.0847   |
| 6        | 0.0810   | 15       | 0.0851   | 25       | 0.0850   |
| 7        | 0.0810   | 16       | 0.0849   | 26       | 0.0846   |
| 8        | 0.0808   | 17       | 0.0838   | 27       | 0.0848   |
| 9        | 0.0801   | 18       | 0.0848   | 28       | 0.0850   |
|          |          | 19       | 0.0840   | 29       | 0.0845   |

$D_{OH} = 435 \text{ kJ mol}^{-1}$ ,  $D_{CH} = 386 \text{ kJ mol}^{-1}$ .

$$\cos \theta = \left\{ \frac{m_1 m_2}{(m_1 + m_2)(m_2 + m_3)} \right\}^{1/2} \quad \cos \theta \begin{cases} (\text{CO, OH}) = 0.1588 \\ (\text{CO, CH}) = 0.1265 \\ (\text{CH, OH}) = 0.9321 \end{cases} \quad (18)$$

where  $m_i$  are the masses of the atoms which form the corresponding bonds.

It should be noted that the  $R$  values thus determined are not accurate since the bond lengths vary with the compounds and should be sensitive to the type of substituent.

The relevant spectral, kinetic and photochemical experimental data are listed in Tables 4 and 5.

## 2. Results and discussion

### 2.1. Effect of the reaction coordinate $R$

In Table 6 are listed the results from calculations of  $R$  using the experimental values of  $E_{e1}$  and  $k_r$  (Tables 4 and 5), eqns. (1), (15) and (16) and constant values of the bond energies ( $D_{OH} = 435 \text{ kJ mol}^{-1}$  and  $D_{CH} = 386 \text{ kJ mol}^{-1}$  (*vide infra*)).

It is readily seen that the structurally similar compounds 1 - 9 (series A) and 10 - 29 (series B), with compounds 4 and 5 being the only exceptions, are characterized by constant reaction coordinates:  $R = 0.0807 \pm 0.0004 \text{ nm}$  (series A);  $R = 0.0848 \pm 0.0004 \text{ nm}$  (series B). Moreover, these values, although slightly higher, are not much different from the  $R$  value obtained from the geometrical models (Figs. 1 and 2,  $R = 0.075 \text{ nm}$ ).

This result indicates that the substituents within a given group (series A or series B) do not affect the displacement coordinate  $R$ .



TABLE 7

Calculated  $D_{\text{OH}}$  values reproducing the experimental rate constants with  $D_{\text{CH}} = 386 \text{ kJ mol}^{-1}$ ,  $R = 0.0807 \text{ nm}$  (series A) and  $R = 0.0848 \text{ nm}$  (series B)

| Series A                 |                                      | Series B |                                      |          |                                      |
|--------------------------|--------------------------------------|----------|--------------------------------------|----------|--------------------------------------|
| Compound                 | $D_{\text{OH}} (\text{kJ mol}^{-1})$ | Compound | $D_{\text{OH}} (\text{kJ mol}^{-1})$ | Compound | $D_{\text{OH}} (\text{kJ mol}^{-1})$ |
| 1                        | 437.2                                | 10       | 439                                  | 20       | 415 <sup>a</sup>                     |
| 2                        | 427.2                                | 11       | 436                                  | 21       | 442                                  |
| 3                        | 436.2                                | 12       | 433                                  | 22       | 435                                  |
| 4                        | 471.2                                | 13       | 429                                  | 23       | 437                                  |
| 5                        | 443.4                                | 14       | 433                                  | 24       | 449 <sup>a</sup>                     |
| 6                        | 449.4                                | 15       | 437                                  | 25       | 430                                  |
| 7                        | 441.0                                | 16       | 434                                  | 26       | 435                                  |
| 8                        | 428.8                                | 17       | —                                    | 27       | 428                                  |
| 9                        | 458.3                                | 18       | 412 <sup>a</sup>                     | 28       | 436                                  |
|                          |                                      | 19       | 430                                  | 29       | 432                                  |
| Average $443.5 \pm 14.3$ |                                      |          | Average $434 \pm 4$                  |          |                                      |

<sup>a</sup>Not included in the averaging procedure.

## 2.2. Effect of the bond energies

The substituents within a series may be expected to affect the bond energies  $D_{\text{OH}}$  and  $D_{\text{CH}}$  because of differences in their nature and in the extent of the resonance effect on the conjugated systems. Unfortunately no data on  $D_{\text{OH}}$  and  $D_{\text{CH}}$  for the compounds studied are available in the literature.  $D_{\text{CH}}$  may be assumed to be constant since all the compounds studied are weak CH acids.  $D_{\text{OH}}$ , however, could vary and we shall try to assess this variation and its effect on the reaction rate constants.

To calculate  $D_{\text{OH}}$  from the experimental  $k_r$  value, we used  $D_{\text{CH}} = 386 \text{ kJ mol}^{-1}$  (as quoted in refs. 6 and 12 for some  $\beta$ -diketones),  $E_{\text{e1}}$  values, averaged  $R$  values (Table 6) and eqns. (15), (16) and (1). The results obtained are listed in Table 7. It can be seen from this table that the experimental  $k_r$  values for series B may be reproduced using a single  $D_{\text{OH}}$  value ( $434 \pm 4 \text{ kJ mol}^{-1}$ ), which is rather close to  $D_{\text{OH}}$  values for secondary and tertiary alcohols ( $D_{\text{OH}} = 433 \text{ kJ mol}^{-1}$ ) [12, 13]. The rate constants for series A, however, show a marked dependence on  $D_{\text{OH}}$  (Fig. 4). The correlation equation is

$$\log k_r = 8.95 - 0.02788D_{\text{OH}} \quad (19)$$

with a correlation coefficient  $r = -0.9325$ .  $D_{\text{OH}}$  is in units of kilojoules per mole. The plot in Fig. 4 shows the expected trend: the rate constant increases with decreasing  $D_{\text{OH}}$  as should be the case if the rupture of the OH bond is involved in the rate-determining stage.

That the rupture of the OH bond is of importance in the reaction process may also be seen from the correlation between the  $\text{pK}$  values (taken from ref. 14) and the  $D_{\text{OH}}$  values from the experimental fit to the photo-

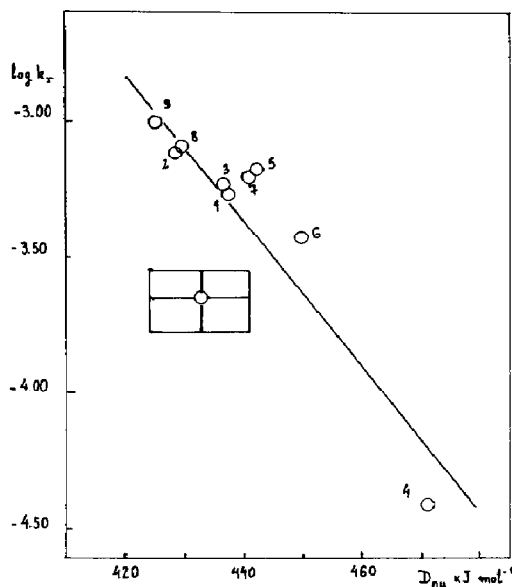


Fig. 4. Correlation between  $\log k_r$  (Tables 4 and 5) and  $D_{OH}$  needed to reproduce  $k_r$ . The numbering of the compounds is given in Table 4. The square represents the 20 points provided by series B (Table 5).  $D_{OH} = 386 \text{ kJ mol}^{-1}$ ,  $R = 0.0807 \text{ nm}$  (series A) and  $R = 0.0848 \text{ nm}$  (series B).

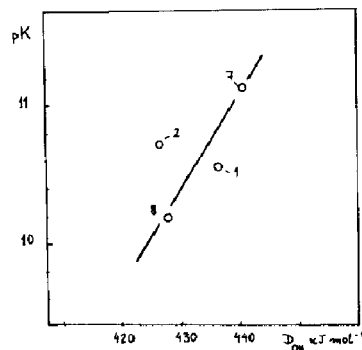


Fig. 5. Correlation between pK of the enol forms and the energy of the OH bonds in these enol forms needed to reproduce the experimental rate constants (Table 4).

ketonization reaction rate constants (Fig. 5). The lower pK values are found for the weaker OH bonds, thus confirming the expected easier release of hydrogen for the stronger OH acids and the more reactive  $\beta$ -dicarbonyls.

Another approach to finding the missing bond energies would be [15] to start with a parent compound and to use  $D_{OH} = 435 \text{ kJ mol}^{-1}$  to evaluate  $R$ , which could then be kept constant for the series under consideration. For the remaining compounds of this series  $D_{OH}$  may be found from a correlation between  $k_r$  and  $D_{OH}$ .

To use this approach, however, we must be sure that the  $R$  value is virtually constant for the given series. In our case we have proved this assumption (see Table 6). In general this may not be valid and each series should be treated separately in the determination of the  $R$  value(s).

### 2.3. Comments on the reaction mechanism

The idea that the primary process in the photoketonization reaction, in which an unstable enol rotamer is formed, is a photoisomerization reaction was stated for the first time in ref. 16. In a more specific form and based on experimental data this idea has been elaborated by Veierov *et al.* [11]. The keto form is considered to be formed thermally from the unstable enol rotamer. Recently Kittel *et al.* [17, 18] have shown that the photoketonization in acetoacetic ester solutions may also proceed as a result of triplet energy transfer from aromatic hydrocarbons to the  $\beta$ -dicarbonyl system.

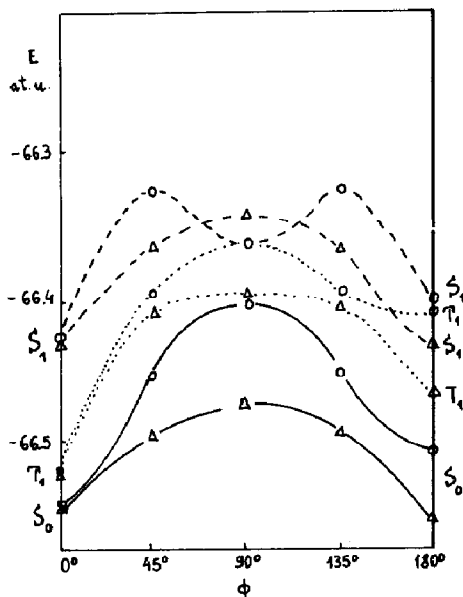


Fig. 6. Variation of the energy of the ground state  $S_0$ , the first excited singlet state  $S_1$  and the first excited triplet state  $T_1$  of compound 1 with the angle  $\phi$  of rotation about the C(3)—C(4) ( $\circ$ ) and C(2)—C(3) ( $\Delta$ ) bonds [19] (see Fig. 1).

We consider that the triplet-excited enol rotamer is the immediate precursor of the keto form. The triplet excited state is formed via excitation of the first excited singlet and subsequent internal conversion. The lifetimes of the first excited singlets (Tables 4 and 5) for the enol forms were found to be almost constant and very low (approximately  $2 \times 10^{-9}$  s). Consequently, the internal conversion (radiationless transition) leading to the population of the first excited triplet must occur for a very short time with a very high rate. Such a rate may occur only when the two curves (singlet and triplet) cross each other. In fact such a crossing has been found [19] using complete neglect of differential overlap spectroscopy calculations for the  $90^\circ$  rotamer of compound 1 which is formed by rotation about the C=C bond (Fig. 6). For triplet-singlet curve crossing the internal conversion rate constant  $k_{ic}$  is known [20] to be of the order of  $10^{-7} - 10^{-11} \text{ s}^{-1}$  which is sufficiently high, compared with the lifetime ( $10^{-9}$  s) of the first excited singlet, to effect the radiationless transition.

From this point of view, the stages  $S_0 \rightarrow S_1$  and  $S_1 \rightsquigarrow T_1$  are not rate determining. The rate-determining step is probably the next stage  $T_1(E) \rightarrow S_0(K)$  where E and K denote the enol and keto forms respectively. The hydrogen abstraction taking place at this stage can occur through the reaction space even though the energy barriers involved (judging from the very low values of the overlap integrals for the atomic orbitals of the two reaction sites (CH and OH)) are very high [3]. For this reason the tunnelling of the hydrogen atom may be highly preferable to reaction over the energy barrier. In fact the successful treatment reported here of the kinetic data for the

photoketonization of  $\beta$ -dicarbonyl compounds by the tunnel effect theory of radiationless transitions suggests that this might be the case.

In this treatment, however, we used the singlet energy because the triplet energy is not known. The difference  $E(S_1) - E(T_1)$  is probably constant and not too large. Thus the use of the singlet energy instead of the triplet energy would not affect the general conclusions reached in this paper, although the estimated  $R$  values would be lower than those found from the analysis of the kinetic data [15].

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