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Short Communication

On the competition between six and seven centre abstractions in the photochemical type II process

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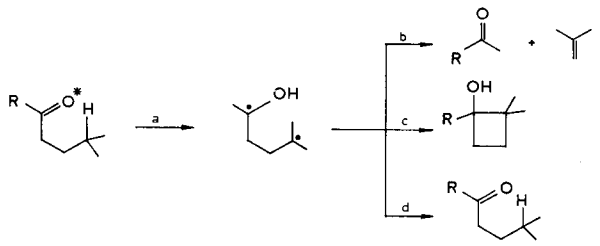
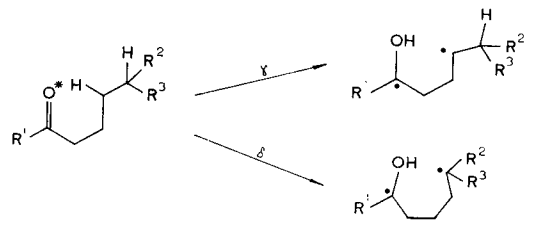
Carbonyl compounds bearing γ-hydrogen atoms usually undergo intramolecular hydrogen abstraction, ultimately leading to Type II photofragmentation and photocyclization products[1]:



(1)

If the δ position is activated, for example by introduction of suitable substituents, γ and δ abstractions can be made to compete intramolecularly[2]:



(2)

Using a semi-empirical method which we have reported elsewhere[3–7], we have carried out a series of calculations of the expected reactivity at the two positions, for several values of bond dissociation energies. We have assumed that the difference in A factors results exclusively from (a) the replacement of four (δ-abstraction), rather than three (γ-abstraction) internal rotations by out-of-plane torsions, and (b) the ratio of path degenerancies ($\sigma_\delta/\sigma_\gamma$). The latter can be calculated as the ratio of equivalent abstractable hydrogen atoms at the δ and γ positions

respectively. The difference in activation energies at the two positions was estimated using a modified bond energy–bond order (BEBO) method[4,5], and assuming that the activation energy at each position is the same as for an intermolecular abstraction with the same thermochemical parameters. Moreover, we assume that both abstraction rings, six and seven centre, are strain-free. In the case of γ abstraction these assumptions have been shown to hold, and are supported by the agreement between experimental and calculated kinetic parameters[6–8].

The calculations presented herein do not take into account the possibility of changes in reactivity resulting from changes in electrostatic interaction and/or the nature of the excited triplet state.

The results for D (γ C–H) values of 91 and 94 kcal/mol (typical tertiary and secondary C–H bonds) are shown in Fig. 1 as a function of the δ-bond dissociation energy. Other thermochemical and spectroscopic parameters are the same as in previous calculations[5,6]. The difference $E_t - E_a$ was taken as -1.0 kcal/mol, and the entropy loss associated with the loss of an additional internal rotation as -4 e.u./mol, in order to be consistent with our previous calculations[6].

In order to obtain the calculated ratio of reactivities from Fig. 1, the value of k_δ^0/k_γ^0 must be multiplied by the ratio of path degenerancies, *i.e.*

$$\frac{k_\delta}{k_\gamma} = \frac{k_\delta^0}{k_\gamma^0} \cdot \frac{\sigma_\delta}{\sigma_\gamma} \tag{3}$$

We note that if the path degenerancy is the same at the two positions the difference in bond energies required to have similar reactivities is of the order of

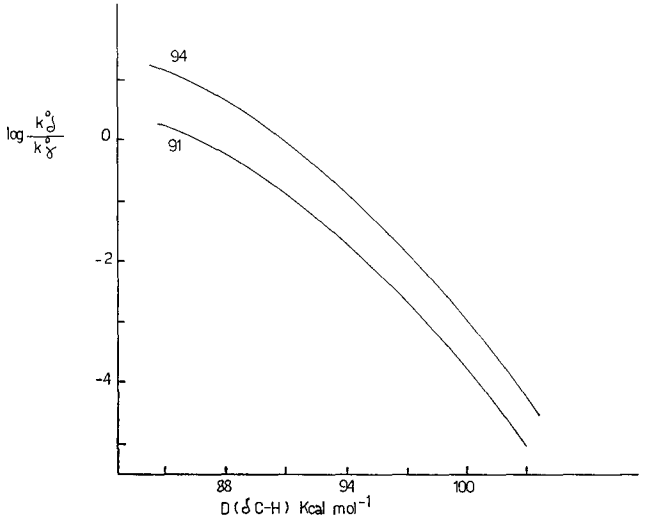


Fig. 1. Relative reactivities at the δ and γ positions for a unity ratio of path degenerancies. The values on the curves indicate the γ-bond dissociation energies in kcal/mol.

3–4 kcal/mol, while for similar bond energies one would expect about 10% of δ abstraction. In the case of valerophenone our calculations suggest that δ abstraction is $\sim$ 0.7%. In all cases we have assumed strain-free abstractions, though we cannot exclude the possibility of small contributions from this factor in some cases.

Wagner *et al.*[9] have examined the effect of substituents on the rates of intramolecular hydrogen abstraction. They conclude that a γ-methoxy group enhances the reactivity at this position by a factor of 4–5, while introduction of a δ-methoxy deactivates the γ-position by about the same factor. Thus, for δ-methoxy valerophenone one can expect the δ-position to be 15–20 times more reactive than the γ-position. This enhancement of the reactivity has been shown to lead to similar reactivities at the two positions[2]. We propose that the main reason why this is so, even when the δ position would be expected to have a higher intrinsic reactivity is that *intramolecular* abstraction at this position has a lower A factor, which results from the loss of four, rather than three internal rotations. On this basis the factor of 15–20 mentioned above must be reduced by a factor of exp (4/RT), *i.e.* we expect the relative reactivity at the δ and γ positions to be around 70:30, in reasonable agreement with Wagner's study of product distribution in this system. Consistently with this, we would expect the δ-position to be considerably more reactive than the γ-position towards *intermolecular* abstraction, *e.g.* by alkoxy radicals.

Finally, we note that similar calculations cannot be expected to be applicable to five-centre abstractions, because processes of this type will probably involve considerable ring strain, and also because the factors which determine the shape of the potential energy profile will be different from those in the case of a co-linear abstraction, which are assumed to hold for six and seven centre abstractions.

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