Photocycloaddition of coumarin and carbostyril to olefins — An intermolecular orbital study

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Abstract. The intermolecular orbital theory of Salem has been used to study the photocycloaddition reactions of coumarin and carbostyril with 1-methoxy ethylene. Theoretical pathways have been drawn for the reactions and the magnitude of the $\pi$-electron stabilisation energy for the reactions has been calculated. All possible cycloaddition patterns have been examined and the relative importance of various interaction terms is discussed. Results of our calculations suggest that the bonds close in a concerted but asymmetric manner. The calculated regioselectivity correlates well with experimental data.

Keywords. Photocycloaddition; reaction pathways; molecular orbital study; coumarins; carbostyrils; olefins.

1. Introduction

Recently, there has been a spurt of interest in cycloaddition reactions of conjugated systems (Song et al 1971; Hammond et al 1964; Hanifin and Cohen 1966; Evanega and Fabiny 1968; Julicn and Foster 1973). Most of these studies were experimental in nature. Earlier theoretical studies were aimed at predicting qualitatively the regioselectivity, i.e. the preferred orientation of these reactions. However, to our knowledge, no attempt has yet been made to study the mechanistic aspects of photocycloaddition reactions of conjugated heterocyclic ketones like coumarin and carbostyril.

In the present work, we have investigated the photochemical reactions of coumarin and carbostyril with 1-methoxy ethylene. We have used the intermolecular theory of Salem (1968a) to predict the most favoured pathway and the preferred orientation of these reactions.

We have deliberately selected an unsymmetrical olefin, i.e., 1-methoxyethylene for our study to illustrate the regioselectivity of the cycloaddition reactions. A comparison of the reaction paths for coumarin and carbostyril would illustrate the effect of substituting the oxygen atom in the heterocyclic ring of coumarin with a nitrogen atom. Moreover, the steric factors in the two systems are the same, while the electronic factors differ sufficiently for us to make a direct comparison.
2. Theoretical methods and models

The energies of interaction between the excited ketone and the ground state olefin have been estimated in terms of the perturbational treatment proposed by Salem (1968a). The π-electronic charges and energies of molecular orbitals, required for the calculation, have been computed by the Pariser–Parr–Pople (PPP) method (Pariser and Parr 1953; Pople 1953).

In Salem’s approximation, the interaction energy between two conjugated molecules is described in terms of the π-electrons of the separate systems. An analytical expression for the interaction energy is obtained as a function of the overlaps between the 2p\textsubscript{z} atomic overlaps of the two molecules.

This method makes use of three main assumptions. Firstly, the σ orbitals of both the molecules are not considered to take part in the reaction. The σ bonds act only as a hard core which does not permit too close an approach. Secondly, each atomic centre is thought to interact with only one centre of the other molecule. The overlap integrals are assumed to be small compared to unity (i.e., \(\leq 0.2\)).

Figure 1 illustrates the energy level diagram for the excited ketones (\(\psi\rightarrow\psi\_r\) configuration) and 1-methoxy ethylene. It is obvious that the highest occupied MOs (HOMOs) of coumarin and carbostyril are nearly degenerate with the

![Figure 1](image)