Study of the thermal decomposition of 3-cyclopentenone by using the AM1 semiempirical method

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Summary. RHF/AM1 and UHF/AM1 low-dimensionality surfaces were calculated by applying the reaction-coordinate technique to the thermal decomposition of 3-cyclopentenone. Several stationary points were accurately located within the entire coordinate space. Although the two formalisms used predicted asynchronous reaction pathways for the process, our results illustrate the limitations of single reference treatments of “two-bond” reactions while the nature of the reaction path remains uncertain.

Key words: Thermal decomposition – 3-cyclopentenone – AM1 – Transition states

1 Introduction

Some aspects of two-bond pericyclic reactions such as the symmetry or asymmetry of the transition state, the concerted or nonconcerted nature of the process, the rationalization of the effects of substituents, etc., have aroused great interest among chemists. One such reaction, viz. the Diels–Alder (DA) prototype reaction, owing to its versatility in organic syntheses, has been the subject of much theoretical and experimental research.

Theoretical studies on the DA reaction [1] have aroused much discussion regarding the computational method to be used rather than the chemistry of the process. In this respect, the use of semi-empirical methods in theoretical studies of two-bond reactions, which was occasionally questioned in the past, has been revitalized by Choi et al. [1] as a consequence of the appearance of the AM1 method, whose predictions for the DA reaction coincide with those from ab initio calculations at the 3–21 G or a higher level (e.g. RHF/AM1 calculations are consistent with the CASSCF 4–31 G results of Bernardi et al. for a synchronous transition state in DA reactions [2, 3]). In the opinions of Choi et al., the AM1 method is an affordable choice for studying this type of reaction, particularly when large zones of the potential hypersurfaces involved are to be explored.

We therefore believed it of interest to use the AM1 method in a theoretical study of cheletropic reactions and, specifically, the elimination of carbon monoxide...
from 3-cyclopentenone (Scheme 1), which had previously been investigated [4–6] by using the MINDO/3 and MNDO methods. Cheletropic reactions [7] are two-bond reactions where the two sigma bonds involved in the process, viz. C₂–C₃ and C₂–C₄, share one atom of one of the reactants (two in the DA reaction).

2 Computational method

Calculations were carried out by using the AM1 method [8] as implemented in the program MOPAC 6.0. Both the RHF and UHF formalism [9] were employed in the search for potential-energy surfaces (PES).

The approximate locations of stationary points on the PES were first determined by using the reaction-coordinate method, according to which the energy of the supermolecule can be expressed as a function of only the two geometric variables that should make the greatest contributions to the actual process coordinate. The variables selected for this purpose were the C₂–C₃ (R₁) and C₂–C₄ (R₂) interatomic distances. All other geometric parameters were optimized at each pair of (R₁, R₂) values in order to minimize the energy of the system.

RHF and UHF grid searches were carried out at R₁ and R₂ variations from 1.4 to 4.5 Å, using an increment of 0.1 Å or smaller in some regions of special interest. The stationary points thus obtained were subsequently refined by minimizing the Euclidean norm of the gradient energy [10] down to below 0.1 kcal mol⁻¹ Å⁻¹, and then characterized by calculating the associated force constants.

3 Results and discussion

3.1 RHF/AM1

Figure 1 shows the RHF/AM1 surface obtained for the thermolysis of 3-cyclopentenone and Table 1 lists the stationary points located after refining from the surface points.

As can be seen in Fig. 1, there is a broad valley from which the reactants can rise in order to be converted into products with the energy requirements for the synchronous and asynchronous modes being quite similar. The zone of the synchronous diagonal maximum (R₁ = R₂) was investigated in greater detail by calculating a denser point network (by increasing R₁ and R₂ by a 0.01 Å interval between 1.8 and 2.2 Å). The surface thus obtained showed a single maximum with a very small curvature in the direction of the asynchronous diagonal. No transition state (TS) of C₅ symmetry such as that obtained by Choi et al. [1] using the same methodology for the DA reaction was found.

A subsequent analysis of the zone by using conjugate gradient methods revealed the presence of three saddle points. The first such point (S₁), where the