Ab initio Calculations on the Electrocyclic Transformation of the Cyclopropyl Radical to the Allyl Radical

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Summary *Ab initio* calculations indicate that the ring-opening of the cyclopropyl radical is formally forbidden in both the conrotatory and disrotatory modes, but that if distortion of the molecule occurs a near-disrotatory reaction would be preferred.

THE electrocyclic ring-opening of a cyclopropyl species is of interest as the simplest reaction which may be treated theoretically by the Woodward–Hoffmann rules.[1] During the reaction the methylene groups may move in either a disrotatory or conrotatory fashion, and one or other mode is preferred depending on the number of electrons present. However, unlike the case of the cation and anion, no conclusion may be drawn from qualitative arguments[1,2] about the mode of reaction of the radical. Moreover, no experimental evidence is available. Extended Hückel calculations[3] predict conrotatory ring-opening, but the MINDO/2 method indicates a disrotatory mode.[4] In this work the reaction is studied by the more accurate Hartree–Fock method, since the MINDO method, although parameterised to reproduce experimental heats of formation, has some defects; in particular, strain energies (*e.g.* in the cyclopropyl ring are underestimated, and the variation of energy with bond length is not well reproduced).

The molecular geometries used, apart from the C–C bond length, were taken from previous calculations on the cation and anion reactions.[5] The C–H length was 2·04 a.u. (allyl) or 2·08 a.u. (cyclopropyl). The bond angles were all 120° for the allyl species, and 60° (CCC) and 116° (HCH) for the cyclopropyl species. Calculations were carried out using the ATMOL/2 System,[6] using a basis set of 60 gaussian functions, contracted to approximate a minimal basis set of Slater-type orbitals. The Slater exponents were as follows: H 1s 1·0, C 1s 5·673, C 2s 1·608, C 2p 1·568.

Previous *ab initio*[5] and MINDO[4] calculations disagree as to whether the cation rearrangement requires activation, and this has been attributed to the use of an assumed geometry for the cyclopropyl species.[4] The variation of energy with the length of the C–C bond was therefore examined; for the allyl species an optimum distance of 2·71 a.u. was found, while for the cyclopropyl species the distance of minimum energy is 2·93 a.u. The geometries of configurations intermediate between allyl and cyclopropyl were obtained by linear interpolation; the rotation of the methylene groups out of the plane of the carbon atoms was used as a reaction co-ordinate. The methine hydrogen was kept in this plane.

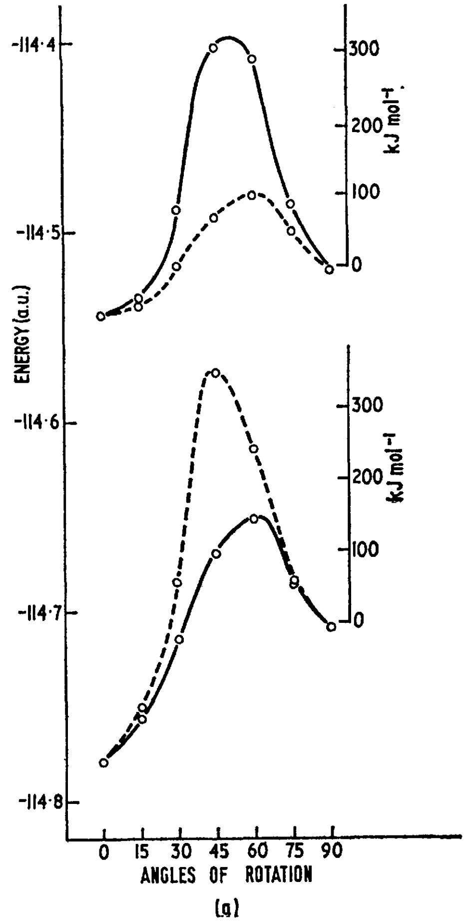

FIGURE 1. *Energy profiles for the cyclopropyl* (90°) *to allyl* (0°) *interconversion. The upper curves are for the cation, the lower curves for the anion. The full line represents the conrotatory mode, and the broken line the disrotatory mode.*

The change[3] in energy along the reaction co-ordinate for the cation and for the anion are shown in Figure 1. The major difference between our results and those of previous *ab initio* calculations,[5] apart from the improvement in all of the energies, is the stabilisation of the cyclopropyl ions, resulting in higher barriers to ring-opening; this may be attributed to the optimisation of geometry. However, the calculated activation energies (104 kJ mol^{-1} for the cation and 149 kJ mol^{-1} for the anion) are probably overestimated since the geometry has not been optimised for the intermediate stages. The calculations on the radical show that in the ground state the odd electron is in an orbital of a_2 symmetry in the allyl radical, but in a b_1 orbital in the cyclopropyl radical (both species have C_{2v} symmetry). Even though some of the symmetry is lost in the intermediate stages (the conrotatory mode maintains C_2 symmetry, and the disrotatory mode C_s symmetry), these two orbitals always belong to different representations of the appropriate point group, and therefore do not correlate with each other. If methylene groups moved completely symmetrically, it would be expected that the transformation of one radical would produce an excited state of the corresponding symmetry of the other radical, *i.e.* the reaction would be "forbidden" in either mode. Interaction between the two states is possible only if some distortion of the molecule occurs. For example, the methine hydrogen could distort from the rotation axis or out of the symmetry plane, or the methylene groups might move asymmetrically.

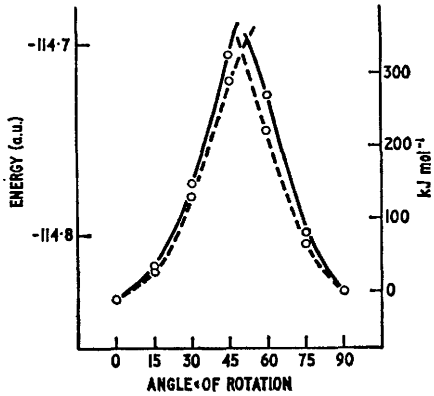

FIGURE 2. *Potential energy curves for the radical reactions.*

The calculated potential energy curves, which are shown in Figure 2, indicate that the overall internal energy change for the ring-opening reaction is appreciably less than that found for the ions; the cyclopropyl radical is predicted to be almost as stable as the allyl radical. These curves would bear a close resemblance to a "real" energy profile for the reaction only if an interaction of the type suggested were small. If this were so, the curves indicate that a near-disrotatory process would be preferred to a near-conrotatory process; this is in accord with the MINDO calculations. However, the reaction might still be very slow, if the interaction between the potential curves were small, since the activation energy for ring-opening would be greater than 250 kJ mol^{-1}, *i.e.*, approaching three times those of the ions. Thus it is quite likely that a more favoured reaction path would be used that cannot be described simply as conrotatory or disrotatory. However, our calculations do not give any indication of what this path might be, or indeed if it exists at all.

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