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COMPETITION BETWEEN CONCERTED AND NON-CONCERTED PATHWAYS IN SYMMETRY-FORBIDDEN REACTIONS

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Orbital symmetry considerations have proven to be a satisfactory general way of predicting the stereochemical outcome of concerted reactions[1]. Controversies persist, however, over the "concertedness" of observes processes for which no allowed alternatives exist[2]. We here open the problem of stabilising the transition states of forbidden, concerted modes so that they become energetically accessible and can compete with non-least motion modes or non-concerted pathways involving spin-unpaired intermediates.

Consider a hypothetic spin-paired system A $\rightleftharpoons$ B which interconverts thermally, along a given coordinate R, in the concerted, symmetry-forbidden fashion. This implies that the system remains in its totally symmetric ground state for all values of R. We presume that no interactions between non-bonded atoms or groups prevent the system from reaching the transition state. R_A and R_B are the equilibrium values of R for the stable reactant(s) A and product(s) B, H_A and H_B their enthalpies, k_A and k_B their harmonic force constants with respect to R. The dagger (‡) denotes the characteristic quantities of the transition state. Since A and B have by definition different electronic configurations, their potential energies $V_A(R)$ and $V_B(R)$ with respect to a deformation along R can be expressed in the harmonic force field approximation as follows:

$$V_A(R) = k_A/2\,(R - R_A)^2 + H_A\,; \qquad V_B(R) = k_B/2\,(R - R_B)^2 + H_B\,.$$

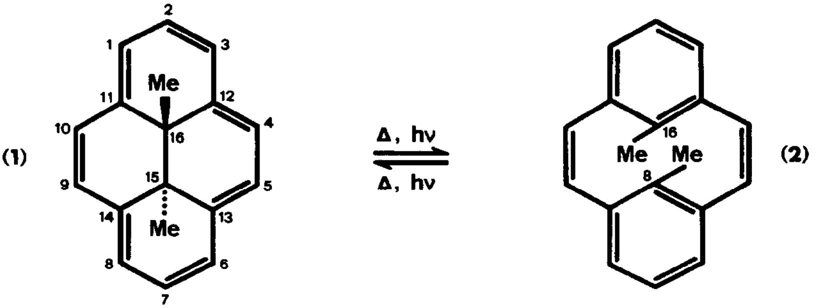
The crossing point of the two parabolas defines the transition state. $\Delta H^{\ddagger}$ and $R^{\ddagger}$ can thus be estimated by solving simply the quadratic equation:

$$(R^{\ddagger} - R_A)^2 - k_B/k_A\,(R^{\ddagger} - R_B)^2 - 2\,\Delta H/k_A = 0 \qquad (\Delta H = H_B - H_A).$$

The "harmonic" activation energy represents, for the following reasons, an upper limit: (i) the assumption of a harmonic force field is valid only for relatively small deviations from the equilibrium values of R; (ii) as $V_A(R)$ and $V_B(R)$ have the same total symmetry, first-order configuration interaction is to be expected in the crossing point.

Our crude model suggests methods by which stabilisation of the "concerted" transition state may be achieved: (i) by lowering k_A and/or k_B, (ii) by increasing the anharmonicities of the potential curves, (iii) by reducing the difference $|R_B - R_A|$, and (iv) by stabilising the reaction product(s) at the expense of the reactant(s). Alternatively, one may destabilise the open-shell intermediates and the "non-least motion" transition state.

A likely candidate which combines these electronic and structural features is trans-15, 16-dimethyldihydropyrene (1)[3]. The disrotatory opening of the bond C15-C16 and the 1, 5-sigmatropic methyl group shift - both allowed processes - are ruled out for structural reasons. (1) can be converted photochemically into 8, 16-dimethyl-[2.2]metacyclophane-1, 9-diene (2) which reacts back into (1) in a thermal first-order reaction[4]. The ease of this conrotatory process ($\Delta H^{\ddagger}_{2\rightarrow1}$ = 22.4 kcal/mole; $\Delta S^{\ddagger}_{2\rightarrow1}$ = -7 cal/deg mole) contrasts with the high activation energies of related forbidden reactions, e.g. the disrotatory opening of dimethylbicyclo-[0.2.3]heptene which proceeds slowly even at 400° and possibly non-concertedly[5] The observed frequency factor ($A = 10^{13.6}$ min^{-1}) is typical for normal unimolecular singlet reactions and thus rules out the intermediacy of diradicals and triplet states. We shall now show that of the remaining mechanistic



alternatives - concerted and non-least motion path - only the former is consistent with these findings.

If we relate the coordinate R simply to the distance C15-C16, we obtain from the known structures[6] of (1) and (2): $R_1 = 1.540$ Å, $R_2 = 2.574$ Å. ΔH was determined[4] as 5.6 kcal/mole. For k_1 we use the CC stretching force constant of ethane[7] (4.5 mdyne/Å). As k_2 is essentially a torsional force constant, we may safely assume $k_2 \ll k_1$. With $k_2 = k_1/5$ we calculate from the above equations: $R^{\ddagger} = 1.88$ Å, $\Delta H^{\ddagger}_{2\rightarrow 1} = 31$ kcal/mole. The latter figure, which is surprisingly close to the experimental $\Delta H^{\ddagger}_{2\rightarrow 1}$, reduces further if configuration interaction and the anharmonicities of the potential curves are taken into account. In particular, this anharmonicity must be substantial in view of the low excitation energies in (1) and (2). At least one of the excited singlet states has the same symmetry as the ground state, and its energy exhibits in the vicinity of R_1 a strongly negative and near R_2 a strongly positive gradient with respect to R[8]. On the other hand the severe distortions demanded by a non-least motion path would necessitate a much higher $\Delta H^{\ddagger}_{2\rightarrow 1}$, although such a process would profit from a lower k_1.

The widely accepted opinion that symmetry-forbidden reactions must necessarily proceed in a non-concerted manner or involve non-least motion paths, seems to rest - as the present results show - on an overestimation of the force constants of chemical bonds. As can be inferred from the above equations, the elongation of a CC bond by 0.3 Å requires not more than 29 kcal/mole; if only 0.2 Å are necessary to reach the transition state, the activation energy drops to 13 kcal/mole.

This leads us to believe that the majority of the hitherto observed forbidden processes are indeed concerted, if they require the opening of only one CC bond. However, if two bonds have to be broken, the merits of a non-concerted pathway are obvious[2] (e.g. cyclobutane ⟶ 2 ethylene). On the other hand, incorporation of the ethylene into a large delocalised π system (as in acenaphthylene) effectively obviates the necessity for generating 1,4-diradicals; now the forbidden $_{\sigma}2_s - _{\sigma}2_s$ process may come to the fore[9]. Likewise substituents which introduce low-lying excited singlet states can dramatically enhance the rates of forbidden reactions by increasing the anharmonicities of the potential curves[8, 10]. As the force constant of a NN single bond is lower than that of a CC bond, the rupture of the former requires less activation energy (for an intriguing example cf. ref.[11]). The release of steric strain in the transition state, that is, a strongly negative ΔH, is certainly the driving force in the opening of small ring systems, e.g. cis-[2.2.0] bicyclohexadiene → benzene. Three-membered rings have the added advantage that the initial and final values of R cannot differ, on structural reasons, by more than 0.3 - 0.6 Å; this implies a low activation energy even in the absence of a strongly negative ΔH or a substantial anharmonicity. The recent observation that sterically restricted oxiranes undergo facile disrotatory ring opening to the corresponding carbonyl ylides[12] can be explained in this way. It should be borne in mind, however, that coupling of the internal coordinates may in certain cases invalidate conclusions based on a harmonic "ansatz".

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References

1 R. B. Woodward and R. Hoffmann, Angew. Chem. Int. Ed. 8, 781 (1969)

2 R. Hoffmann, S. Swaminathan, B. G. Odell and R. Gleiter, J. Amer. Chem. Soc. 92, 7091 (1970); M. J. S. Dewar, Angew. Chem. Int. Ed. 10, 761 (1971)

3 V. Boekelheide and J. B. Phillips, J. Amer. Chem. Soc. 85, 1545 (1963)

4 H.-R. Blattmann, D. Meuche, E. Heilbronner, R. J. Molyneux and V. Boekelheide, J. Amer. Chem. Soc. 87, 130 (1965); H.-R. Blattmann and W. Schmidt, Tetrahedron, 26, 5885 (1970)

5 R. Criegee and H. Furrer, Chem. Ber. 97, 2949 (1964)

6 A. W. Hanson, Acta Cryst. B 18, 599 (1965); A. W. Hanson, to be published

7 G. Herzberg, 'Infrared and Raman Spectra', New York 1945, p. 193

8 W. Schmidt, Helv. 54, 862 (1971)

9 W. Schmidt and D. O. Cowan, to be published; L. A. Paquette and L. M. Leichter, J. Amer. Chem. Soc. 93, 4922 (1971)

10 R. Gompper and G. Seybold, Angew. Chem. Int. Ed. 10, 68 (1971)

11 V. Boekelheide and J. A. Lawson, Chem. Commun. 1558 (1970)

12 D. R. Arnold and L. A. Karnischky, J. Amer. Chem. Soc. 92, 1404 (1970)