The Oxirane Radical Cation

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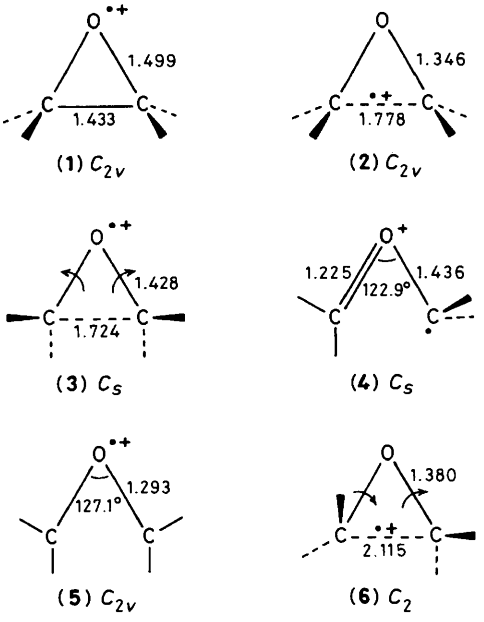
The ${}^2B_1$ and ${}^2A_1$ states of the oxirane radical cation, which are suggested by MP2/6-31G*//6-31G* calculations to be very close in energy, both have small barriers to ring-opening *via* disrotatory and conrotatory processes, respectively.

Recent e.s.r. experiments in freon matrices at 77 K have given spectra which clearly do not correspond to the oxirane cation itself, but rather to a partially[1] or fully[2] ring-opened species. This is an unexpected result as *ab initio* calculations predicted[3] a 24.5 kcal mol^{-1}† barrier to ring-opening. This process was proposed[3] to occur *via* a crossing from the ${}^2B_1$ to the ${}^2A_1$ electronic state. This communication reports higher level calculations‡ which revise the conclusions reached in the earlier study[3] and reveal new features of the oxirane radical cation potential surface, which is connected to the recently investigated vinyl alcohol radical cation system.[4]

The ground state (${}^2B_1$) oxirane radical cation (**1**) arises from removal of an electron from the oxygen π lone pair. The first excited (${}^2A_1$) state (**2**) has a long (1.778 Å) carbon–carbon bond and practically planar carbon centres. This structure is obtained by removing an electron from an orbital with considerable C–C bonding character,[5] and would normally be expected to undergo facile ring-opening. (**2**) was found earlier[3] to be 24.5 kcal mol^{-1} less stable than (**1**), but the inclusion of polarisation functions in the basis set and the MP2 correction results in an enormous stabilisation, reducing the energy difference to 4.2 kcal mol^{-1} at MP2/6-31G*//6-31G*.

Similarly the transition state for the ring-opening of (**1**) [structure (**3**)] is strongly stabilised at MP2/6-31G*. The calculated barrier to ring-opening is only 3.7 kcal mol^{-1} at this level, and may disappear completely at higher levels. The transition state (**3**) shows an initial symmetrical disrotatory ring-opening. At later states in the reaction, however, the structure becomes unsymmetrical and resembles the perpendicular species (**4**), which was found earlier[3] to be the most stable C–C ring-opened form. The all planar structure (**5**) is however found to be 3.8 kcal mol^{-1} more stable than (**4**) at MP2/6-31G*//6-31G*. The asymmetry in the later stages of the reaction allows conversion of the ${}^2B_1$ state (**1**) into the ${}^2A_2$ state (**5**), the reaction being formally forbidden. The low calculated barrier to ring-opening of (**1**) resolves the apparent discrepancy between the earlier theoretical study[3] and the experimental results.[1,2] The calculations also suggest that the experimentally observed species is the planar ${}^2A_2$ radical cation (**5**),[2] as suggested by a recent study on substituted oxirane cations.[6]



Scheme 1

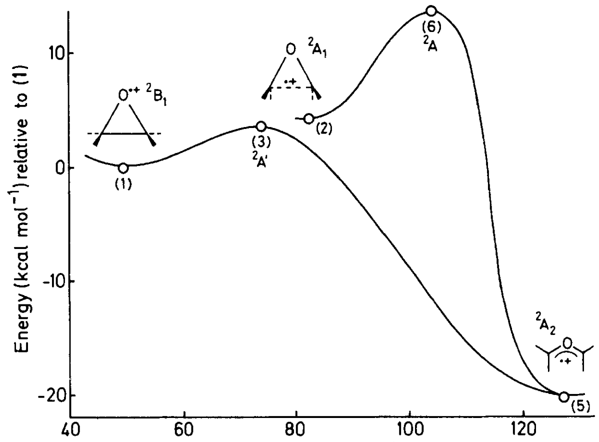


Figure 1

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† 1 kcal = 4.18 kJ.

‡ All calculations used the unrestricted Hartree–Fock formalism and the GAUSSIAN 76 (J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, 'Quantum Chemistry Program Exchange,' Program No. 368, Indiana University, 1978) or GAUSSIAN 82 (J. S. Binkley, M. Frisch, K. Raghavachari, D. DeFrees, H. B. Schlegel, R. A. Whiteside, E. Fluoder, R. Seeger, and J. A. Pople, GAUSSIAN 82. Release A, Carnegie-Mellon University, 1983; modified for CDC computers by Dr. A. Sawaryn) series of programs. Structures (**1**), (**2**), (**4**), and (**5**) were optimised using the 6-31G* basis set (P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213). The transition states (**3**) and (**6**) were located by using the C–O–C angle as a reaction co-ordinate. The two structures thus obtained were confirmed as transition states, and structure (**2**) as a minimum, by diagonalisation of the force constant matrix. These calculations all used the 3-21G basis set (J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939). The 3-21G geometries for (**3**) and (**6**) and the 6-31G* structures for (**1**), (**2**), (**4**), and (**5**) (shown in Scheme 1) were used for single point MP2/6-31G* calculations, which yielded the energies shown in Figure 1. MP2 Calculations (C. Møller and S. Plesset, *Phys. Rev.*, 1974, **46**, 1423; J. S. Binkley and J. A. Pople, *Int. J. Quant. Chem.*, 1975, **S9**, 229; J. A. Pople, J. S. Binkley, and R. Seeger, *ibid.*, 1976, **10**, 1) did not include the non-valence orbitals. All calculations showed little spin contamination ($<S^2>$ less than 0.77) except those for (**5**) ($<S^2>$ = 0.894).

The alternative structure[1] (**2**) is, however, also found to be a local minimum by diagonalisation of the force constant matrix. The transition state for the ring-opening of (**2**) [structure (**6**)] lies 9.5 kcal mol^{-1} higher in energy at MP2/6-31G*. The ring-opening is a conrotatory allowed process, in contrast to the disrotatory forbidden ring-opening of (**1**). The calculated potential surface for the oxirane radical cation system is shown in Figure 1.

The low barrier to the forbidden ring-opening and the fact that (**2**) is a local minimum are both due to an avoided crossing between the $^2A'$ state (in C_2 symmetry) and the $^2A_1$ surface (in C_{2v} symmetry). This avoided crossing, in which the forbidden process takes over the allowed character of the first excited state, facilitates violation of the Woodward–Hoffman rules. These predictions are, in principle at least, experimentally verifiable by stereospecific deuterium labelling of the starting oxirane, but unfortunately the resolution of the e.s.r. spectra is not high enough to distinguish between the two types of hydrogen coupling in (**5**).[1,2]

Non-opened oxirane radical cations may, however, be observable when substituted with groups which preferentially stabilise the $^2B_1$ state relative to the $^2A_1$.

Added in proof: Radom *et al.*[7] have recently published MP3/6–31G*//6–31G* calculations on (**1**), (**4**), and (**5**) which agree with the data reported here.

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References

1 M. C. R. Symons and B. W. Wren, *Tetrahedron Lett.*, 1983, 2315.

2 L. D. Snow, J. T. Wang, and F. Williams, *Chem. Phys. Lett.*, 1983, **100**, 193.

3 W. J. Bouma, J. K. MacLeod, and L. Radom, *J. Am. Chem. Soc.*, 1979, **101**, 5540.

4 Y. Apeloig, M. Karni, B. Ciommer, G. Depke, G. Frenking, S. Meyn, J. Schmidt, and H. Schwarz, *J. Chem. Soc., Chem. Commun.*, 1983, 1497.

5 D. W. Turner, C. Baker, A. D. Baker, and C. R. Bundle, 'Molecular Photoelectron Spectroscopy,' Wiley-Interscience, New York, 1970; K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, 'Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules,' Halsted, New York, 1981.

6 T. Bally, S. Nitsche, and E. Haselbach, *Helv. Chim. Acta*, 1984, **67**, 86.

7 W. J. Bouma, D. Poppinger, S. Saebø, J. K. Macleod, and L. Radom, *Chem. Phys. Lett.*, 1984, **104**, 198.