

Epoxidation of Cyclopentene, Cyclohexene and Cycloheptene by Acetylperoxyl Radicals

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To further the current understanding of how peroxy radicals add to C=C double bonds,^{eg. 1-3} a series of cyclic alkenes (cyclopentene, cyclohexene and cycloheptene) were reacted with acetylperoxyl radicals over the temperature range 373 - 433 K, via the co-oxidation of acetaldehyde, the cyclic alkene and a reference alkene. The resulting epoxides were monitored by GC-FID, allowing the determination of the Arrhenius parameters given in Table 1 for these addition reactions.

Alkene	$\log_{10}(A / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$E_{\text{act}} / \text{kJ mol}^{-1}$
cyclopentene	9.7±0.6	31.2±5.0
cyclohexene	7.7±0.7	17.4±5.3
cycloheptene	8.8±0.8	25.5±6.5
<i>cis</i> -2-butene ⁴	8.1±0.5	22.9±3.8

Table 1: Arrhenius parameters for the addition of acetylperoxyl radicals to cyclic alkenes and *cis*-2-butene.

Parameters for *cis*-2-butene are also given for comparison,⁴ as it would be expected that a relatively unstrained cycloalkene would behave in a similar manner to this non-cyclic alkene; this is indeed found to be so, with no statistically significant difference between cyclohexene and *cis*-2-butene. Indeed the measured activation energy for cyclohexene fits in well with correlation between charge transfer (ΔE_c) and activation energy that is known to exist for the addition of acetylperoxyl to acyclic mono-alkenes.¹

Cyclopentene however does have a significantly larger pre-exponential factor and activation energy than either cyclohexene or *cis*-2-butene. Geometries for the transition states and isolated reactants calculated using MOPAC 6 with the AM1 hamiltonian⁵ indicate that radical addition to the highly strained cyclopentene (which is constrained to be planar) can release a significant amount of entropy, and consequently increase the pre-

exponential factor for the reaction. The calculated ratios of the pre-exponential factors for cyclopentene with respect to cyclohexene ($\log_{10}(A_{C5}/A_{C6}) = 1.8$) is comparable with the experimental determination (2.0 ± 0.9). In comparison with addition to cyclohexene, the transition state for addition to cyclopentene is comparatively early and involves less charge transfer, thus providing an explanation for its higher activation energy.

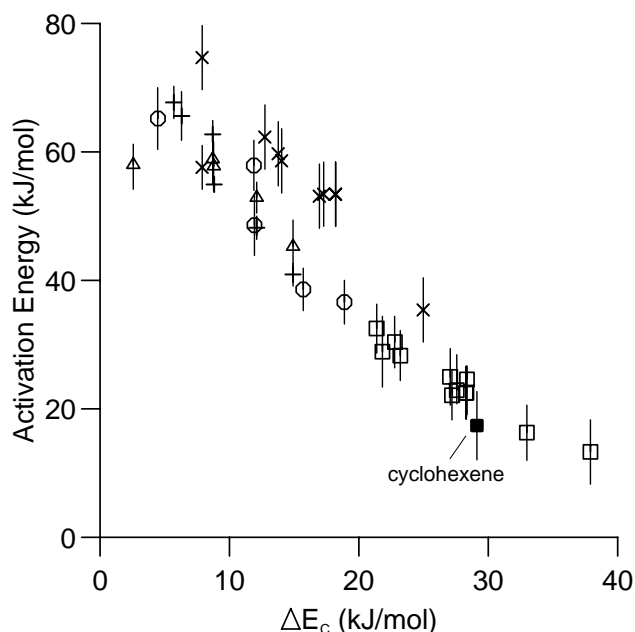


Figure 1. Relationship between ΔE_c and the activation energy for the epoxidation of alkenes by: acetylperoxyl radicals, ■ cyclohexene, □ other monoalkenes.

Other radicals: ○ methylperoxyl: × hydroperoxyl: + *iso*-propylperoxyl: Δ *tert*-butylperoxyl.^{2,3,1}

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