Epoxidation of 2,3-Dimethyl-2-Butene, Conjugated Dienes and 1,5-Hexadiene by Acetylperoxyl Radicals

J. R. Lindsay Smith, D. M. S. Smith, M. S. Stark* and D. J. Waddington
Department of Chemistry, University of York, York, YO10 5DD, United Kingdom

Activation energies for the addition of peroxyl radicals to alkenes correlate well with the energy released by charge transfer to the radical at the transition state (ΔE_c).[1] This correlation (figure 1) has now been extended to the most polar reaction yet studied, the epoxidation of 2,3-dimethyl-2-butene by acetylperoxyl radicals (reaction 1) between 393 and 433 K, via the co-oxidation of acetaldehyde and 2,3-dimethyl-2-butene and a previously studied reference alkene (isobutene).

$$CH_3C(O)O_2\cdot + (CH_3)_2C{=}C(CH_3)_2 \rightarrow CH_3\cdot + CO_2 + (CH_3)_2\overset{\frown}{COC}(CH_3)_2 \qquad (1)$$

The activation energy ($E_1 = 13.3\pm5.0$ kJ mol^{-1}) is consistent with values for other alkenes (Figure 1), while the pre-exponential factor [$\log_{10}(A_1/\mathrm{dm^3mol^{-1}s^{-1}}) = 9.1\pm0.6$] shows no sign of steric hindrance at the relatively crowded double bond, being if anything slightly larger than typical *A* factors for smaller alkenes [$\log_{10}(A_{alkene}/\mathrm{dm^3mol^{-1}s^{-1}}) \approx 8.1\pm0.5$].

A series of conjugated dienes (1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene) and the unconjugated 1,5-hexadiene have also been examined, Arrhenius parameters are given in Table 1. Electron affinities are only available for 1,3 butadiene, so ΔE_c could only be calculated for reaction 2, which is also included on Figure 1.

$$CH_3C(O)O_2\cdot + CH_2{=}CH\text{-}CH{=}CH_2 \rightarrow CH_3\cdot + CO_2 + CH_2{=}CH\text{-}H\overset{\frown}{COC}H_2 \qquad (2)$$

Interestingly, the activation energy for 1,3-butadiene also lies on the line of correlation of the mono-alkenes given in figure 1, in spite of it having a relatively low ionisation energy due to resonance stabilisation of the diene cation (the pre-exponential factor is also comparatively high at $\log_{10}(A_2/\mathrm{dm^3mol^{-1}s^{-1}}) = 9.6\pm0.6$). There is, in effect, no resonance stabilisation of the transition state with respect to the isolated reactants. The activation energy is relatively high because the electron affinity of the diene is also relatively low (due to resonance stabilisation of the diene anion), therefore the *electronegativity* and consequently activation energy of 1,3 butadiene (4.21 eV and 30.9 ± 5.0 kJ mol^{-1} respectively) are similar to propene (3.88 eV and 32.5 ± 3.8kJ mol^{-1}).

Alkene	$\log_{10}(A$ / dm^3 mol^{-1} s^{-1})	E_{act} / kJ mol^{-1}
2,3-dimethyl-2-butene	9.1±0.6	13.3±5.0
1,3-butadiene	9.6±0.6	30.9±5.0
isoprene	8.7±0.9	23.3±6.7
2,3-dimethyl-1,3 butadiene	8.1±1.4	17±11
1,5-hexadiene	9.6±0.8	35.8±6.2

Table 1: Arrhenius parameters for the addition of acetylperoxyl radicals to 2,3-dimethyl-2-butene, selected conjugate dienes, and 1,5-hexadiene.

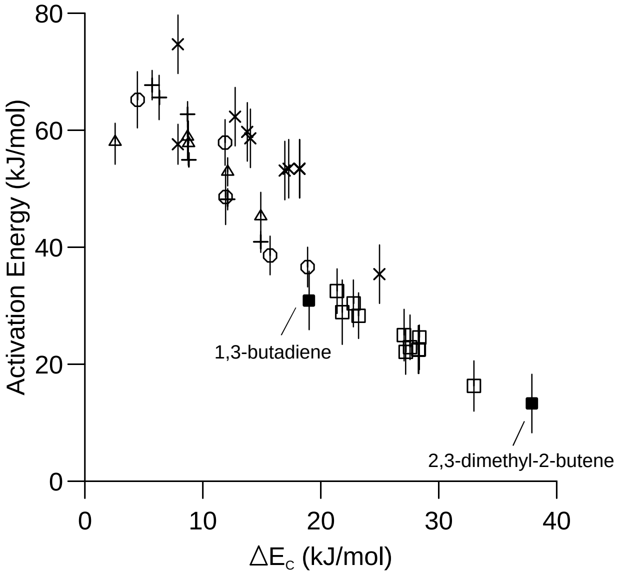

Figure 1. Relationship between ΔE_c and the activation energy for the epoxidation of alkenes by: acetylperoxyl radicals, ■ 1,3-butadiene and 2,3-dimethyl-2-butene, □ other monoalkenes. Other radicals: ○methylperoxyl: × hydroperoxyl: + *iso*-propylperoxyl: △ *tert*-butylperoxyl.[2,3,1]

(1) Stark, M.S. *J. Phys. Chem.* **1997**, *101*, 8296. Stark, M.S., *J. Am. Chem. Soc.*, in press, web published 15th April **2000**.

(2) Ruiz Diaz, R.; Selby, K.; Waddington, D.J. *J. Chem. Soc. Perkin Trans. 2* **1977**, 360.

(3) Baldwin, R.R.; Stout, D.R.; Walker, R.W. *J. Chem. Soc Faraday Trans. 1* **1984**, *80*, 3481.