

## Addition of Peroxyl Radicals to Alkenes and the Reaction of Alkyl Radicals with O<sub>2</sub>

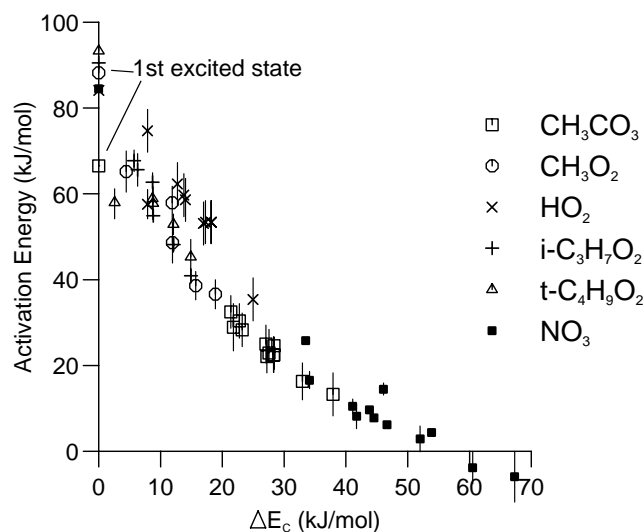
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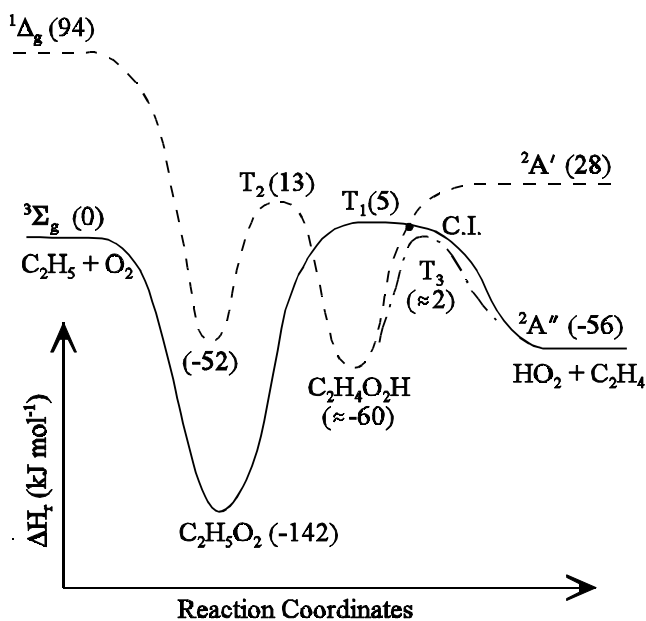
A two state mechanism is proposed for the addition of peroxy radicals to alkenes.<sup>1</sup> The activation energy for the reaction is determined by proximity of the transition state to an unavoided crossing of the ground and first excited states, and if no energy is released by charge transfer, then it is similar to the energy required to excite the peroxy radical from the ground <sup>2</sup>A'' state to the first electronically excited <sup>2</sup>A' state. With charge transfer, the activation energy for the addition is lowered in proportion to the energy released ( $\Delta E_c$ ) by the charge transfer, as shown in Figure 1. The first electronically excited <sup>2</sup>A' state of the peroxy radical correlates to the ground state of the peroxyalkyl adduct, whilst the ground <sup>2</sup>A'' state correlates to an excited state of the peroxyalkyl adduct, with the surfaces crossing at a conical intersection, which is proximate to, and higher than the transition state for the addition (shown schematically for the example of HO<sub>2</sub> + C<sub>2</sub>H<sub>4</sub> in Figure 2). This description is also relevant to other oxygen centred radical additions, notably NO<sub>3</sub>,<sup>eg. 2</sup>, which conforms to the structure-activity relationship observed for the peroxy radicals (Figure 1). It is suggested that the additions of mono or diatomic radicals are essentially barrierless due to their high symmetry.

For the specific case of HO<sub>2</sub> addition to ethene, it has been suggested that the epoxidation mechanism described by Baldwin and Walker<sup>3</sup> contradicts the mechanism for the addition of O<sub>2</sub> to ethyl radicals suggested by Wagner, Gutman *et al.*<sup>4</sup> It is argued that the epoxidation mechanism described here (which is a continuation of that of Waddington,<sup>eg. 5</sup> and Baldwin and Walker<sup>eg. 3</sup>) is entirely consistent with that of Schaefer *et al.*<sup>6</sup> for the addition of O<sub>2</sub> to alkyl radicals and the subsequent decomposition to the conjugate alkene + HO<sub>2</sub> (Figure 2). It appears necessary though to re-examine the barrier heights for the decomposition of C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> + HO<sub>2</sub> (T<sub>1</sub>, Figure 2) and the addition HO<sub>2</sub> + C<sub>2</sub>H<sub>4</sub> to form ·CH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>H (T<sub>3</sub>, Figure 2). It is suggested that T<sub>1</sub> is *ca.* 5 kJ mol<sup>-1</sup> higher than  $\Delta H_{298K}(C_2H_5 + O_2)$  (not 16 kJ mol<sup>-1</sup> below as suggested by Wagner *et al.*<sup>4</sup>) and that T<sub>3</sub> is *ca.* 15 kJ mol<sup>-1</sup> lower than quoted by Baldwin and Walker.<sup>3</sup>

**Figure 1:** Relationship between  $\Delta E_c$  and the activation energy for the addition to alkenes by peroxy and nitrate radicals.<sup>1-4</sup> Energies of the transitions to the first electronically excited states of the radicals are shown on the vertical axis.



**Figure 2.** Schematic potential energy diagram for the  $C_2H_5 + O_2/HO_2 + C_2H_4$  system: solid line  $^2A''$  state; dashed line  $^2A'$  state: C.I., conical intersection; hatched line, transition state.<sup>1</sup>



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