

**P1** *(Invited Lecture)*  
**The Activation Energy of Bimolecular Reactions**

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The potential energy surface (PES) for a chemical reaction determines uniquely the chemical activation energy and the Arrhenius A-factor. After forty years of efforts to predict PES, we can summarize the present situation by saying that we are wiser in knowing how to begin to tackle the problem, but that really quantitative *a priori* calculations are probably still a long way off. However, on the empirical side, there are some really bright spots. Arrhenius A-factors are not too sensitive to the details of the PES, and we can today predict them with accuracy of a factor of  $10^{\pm 0.3}$  which is usually much better than experimental accuracy. This is true of both bimolecular and unimolecular processes.

Activation energies have yielded to empirical approaches in a number of sectors. The Johnston-Parr method of Bond Energy-Bond Order gives  $E_{act}$  for metathesis to about  $\pm 2$  kcal for first-row elements in saturated systems. Recent empirical efforts in the author's laboratory have given a number of extremely simple correlations with average accuracy of about  $\pm 1.2$  kcal (400 reactions) and maximum deviations of 2.6 kcal. These studies suggest that it is the electron affinity of elements (or groups) A and C in the metathesis reaction:



which dominate the value of  $E_{intrinsic}$  (*i.e.*, the activation energy in the exothermic direction). The nature of B and the exothermicity of the reaction seem to play secondary roles.

Recent studies by the author show that a similar analysis holds for the addition of radicals or atoms to unsaturated systems and that one can make some very interesting generalizations about both metathesis and addition reactions which tie them to acid-base reactions, recombination reactions, or donor-acceptor interactions. Also, as anticipated from theory, there is a close relation between A-factor and  $E_{intrinsic}$ . A perhaps surprising

result is that both metathesis and addition reactions can show Arrhenius parameters characteristic of "loose" as well as tight transition states.

**P2** *Chemiluminescence for the Determination of Activation Energies of Hydrocarbon Oxidation*

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Dodecane, tetralin, 1-tridecene, *trans*-decalin, and indane were subjected to chemiluminescence analysis during their oxidation. Studies were carried out over a wide temperature range on pure compounds carefully purified by first extraction with sulfuric acid (with the exception of indane), neutralization, chromatography through silica and alumina, and finally vacuum distillation under argon. Activation energies were obtained for initiation and propagation steps for the oxidation process, most of which were previously unavailable and contribute toward a better understanding of the oxidation mechanism. The research identified the following  $E_{init}$  (for the peroxide decomposition step) for the above compounds:  $16.1 \pm 2.6$ ,  $23.2 \pm 3.6$ ,  $13.5 \pm 3.2$ ,  $12.5 \pm 2.4$ , and  $16.0 \pm 3.6$ , kcal/mole, respectively. In particular the chemiluminescence analysis identified the importance of a unimolecular propagation process prevalent during the high temperature oxidation of dodecane and 1-tridecene.  $2E_{prop} - E_{term}$  were found to be for tetralin, *trans*-decalin, and indane  $24.2 \pm 3.8$ ,  $30.9 \pm 4.8$  and  $30.0 \pm 3.8$  kcal/mole, respectively. For dodecane and tridecene these were found to be  $39.8 \pm 4.0$  (dodecane,  $130 - 160^\circ\text{C}$ ),  $11.4 \pm 3.9$  (dodecane  $170 - 200^\circ\text{C}$ ),  $36.7 \pm 4.3$  (1-tridecene,  $120 - 140^\circ\text{C}$ ), and  $9.8 \pm 4.3$  kcal/mole (1-tridecene,  $140 - 165^\circ\text{C}$ ).

**P3** *(Invited Lecture)*  
**The Study of Free Radicals in the Gas Phase Using Magnetic Resonance**

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