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 ± 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 ± 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:

$$\dot{A} + B{-}C \rightleftarrows A{-}B + \dot{C}$$

which dominate the value of $E_{\text{intrinsic}}$ (*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 $E_{\text{intrinsic}}$. 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 ± 2.6, 23.2 ± 3.6, 13.5 ± 3.2, 12.5 ± 2.4, and 16.0 ± 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. $2E_{\text{prop}} - E_{\text{term}}$ were found to be for tetralin, *trans*-decalin, and indane 24.2 ± 3.8, 30.9 ± 4.8 and 30.0 ± 3.8 kcal/mole, respectively. For dodecane and tridecene these were found to be 39.8 ± 4.0 (dodecane, 130 - 160 °C), 11.4 ± 3.9 (dodecane 170 - 200 °C), 36.7 ± 4.3 (1-tridecene, 120 - 140 °C), and 9.8 ± 4.3 kcal/mole (1-tridecene, 140 - 165 °C).

P3 *(Invited Lecture)*

The Study of Free Radicals in the Gas Phase Using Magnetic Resonance

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In recent years studies of free radicals in the gas phase by electron paramagnetic resonance have mainly used microwave sources in the X-band (ca. 9000 MHz) and the molecules detected have been almost exclusively diatomics in $^2\Pi$, $^3\Sigma$ or $^1\Delta$ states. In recent years, for instance, we have studied OH($^2\Pi$, v = 1 - 5), $S_2(^3\Sigma_g^-)$ and NF($^1\Delta$). This spectral region has, however, proved less useful for polyatomic species and for linear molecules in $^2\Sigma$ states.

However, if the microwave source is replaced by a far infra-red laser operation in the 30 - 120 cm^{-1} range, the Zeeman effect can be used to bring a rotational transition of a free radical into resonance the laser line providing their initial separation does not exceed 2 cm^{-1}. If the free radicals are generated within the laser cavity, the greater energy of the transitions increases the sensitivity by a factor of 1000 as compared with gas phase e.p.r. This is due to the increased transition probability and to the greater difference between the populations of the levels involved. Parallel and perpendicular transitions can be separated by rotating the plane polarisation of the laser beam.

Analysis of laser magnetic resonance spectra can provide structural information about free radicals. Spectra of the ground states of NH_2 and PH_2 are presented, together with spectra of PH($^3\Sigma^-$) and PH($^1\Delta$). The unpaired electron(s) in PH_2 and PH($^1\Delta$) are shown to be largely localised on the $3p$ orbital of the P atom.

This work has been carried out in collaboration with Drs. P. B. Davies, D. K. Russell and F. D. Wayne.

P6

Photochemically Induced Dynamic Magnetic Polarization

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The current theories of chemically induced dynamic magnetic polarization in free radical reactions in carbonyl photochemical systems are summarized in terms of the "radical-pair" and the photoexcited triplet models. Experimental evidence is presented to show the coexistence of both these mechanisms in electron as well as in nuclear polarization. Systematic and correlated CIDEP and CIDNP investigations of the photochemical reactions of quinones and aliphatic carbonyl compounds allow the introduction of a general scheme for the simultaneous operations of the two mechanisms in the photochemical systems.
The primary photochemical reactions contribute to magnetic polarization via the "photoexcited triplet" model, whereas the secondary reactions of the primary radical-pair contribute by the "radical-pair" mechanism. Detailed analysis of the magnetic polarization results would lead to important information on dynamics and mechanisms of intersystem crossing, rates of chemical reactions of the triplet sublevels and the spin-lattice relaxation rates of the triplets and the transient radicals in solution.

P7

Modulated Excitation ESR Spectra of Hydroxy-Phenoxy Radicals

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In a modulated excitation E.S.R. (M.E.S.R.) spectrometer the UV light inducing the photochemical reaction is sinusoidally modulated, so that beside the conventional E.S.R. of the resulting radicals also the phase shift and amplitude of each individual line of the spectrum can be measured. The detection system [1] of such an instrument is schematically shown in Fig. 1.

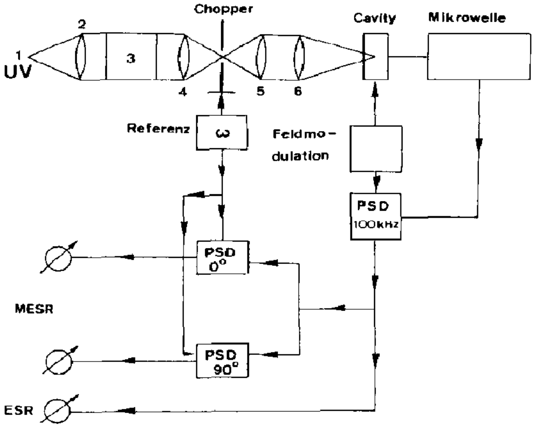

Fig. 1. Detection system of the M.E.S.R. spectrometer.