B1. Predictive Theory for Radical-Radical Kinetics

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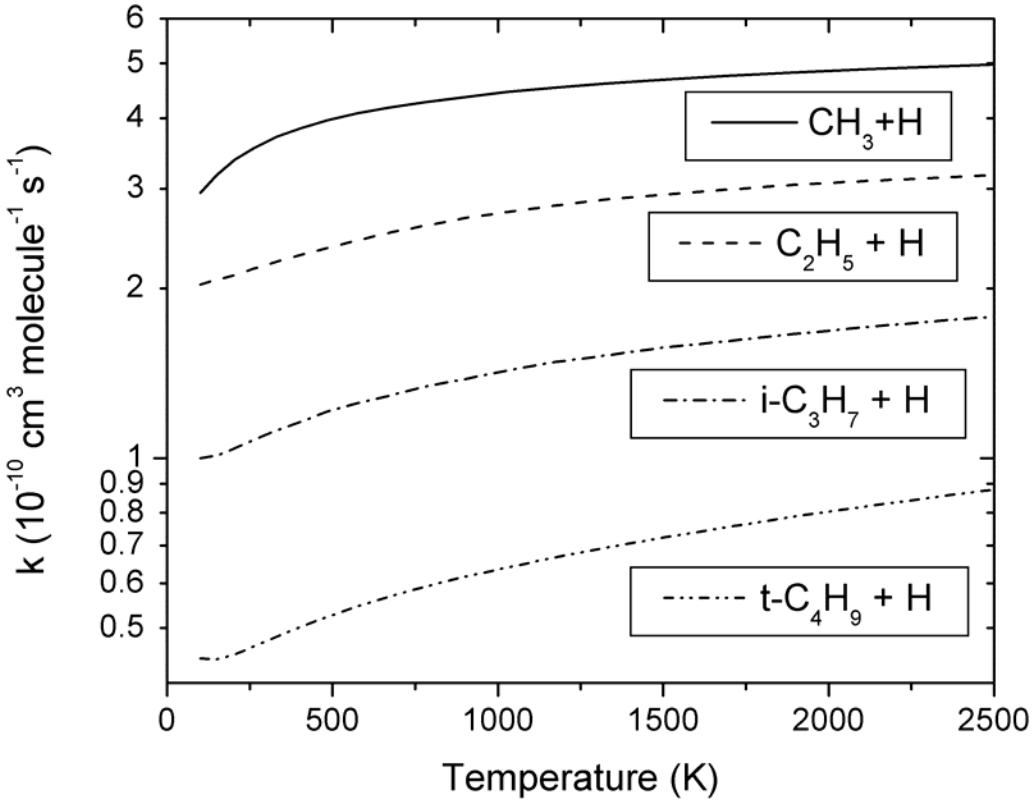
Illustrative applications of a widely applicable procedure for predicting the kinetics of radical-radical reactions will be presented. This procedure is based on the direct implementation of CASPT2/dz energies within variable reaction coordinate (VRC) transition state theory (TST). Higher level corrections are obtained from the difference between CASPT2/dz and MRCI/atz calculations for the smallest chemically similar system. Applications to a series of R + H and R + R′ addition reactions, where R is a hydrocarbon radical, will be used to illustrate the accuracy and generality of the approach.

For the R + H reactions, related MRCI/atz based VRC-TST calculations for R = CH_3, C_2H_5, C_2H_3, and CCH allow for a direct test of the CASPT2/dz based approximations to the potential energy surface. Comparisons with experiment and with trajectory simulations provide a test of the transition state theory assumptions. Calculations for phenyl and naphthyl radicals illustrate the power of this direct VRC-TST approach. For the R + R′ reactions calculations for CH_3 + CH_3 provide a detailed test of the approach.

Consideration of the series R, R′ = CH_3, C_2H_5, iso-C_3H_7, and tert-C_4H_9 provides a test of the geometric mean rule, as well as illustrating the steric effect on the high presure addition rate constants for both R + H and R + R′. For both series, each additional methyl group reduces the rate coefficient by approximately a factor of two. These results also indicate that the rate constants for the R + H reactions generally increase slightly with increasing temperature, whereas those for the R + R′ reactions generally decrease with increasing temperature. For the recombination of two tert-butyl radicals the rate constant is predicted to decrease by a factor of 30 from 200 to 2000 K.



A final series of illustrations considers addition reactions involving resonantly stabilized radicals. The study of these reactions is complicated by the need to consider (i) multiple binding sites, (ii) the effect of resonances in the electronic structure, and (iii) increased geometrical relaxation effects. For this series we present preliminary results for the C_3H_3 + H reaction (as a test of the approach), the C_3H_3 + C_3H_3 reaction, and the H + C_7H_7 reaction. The latter two reactions are of considerable importance in understanding soot formation in combustion chemistry. The study of the H + C_7H_7 reaction is coupled with a related study of the CH_3 + C_6H_5 reaction to yield a pressure dependent analysis of the toluene decomposition process.

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B2. Radical-Radical Reactions Between NCO($X^2\Pi$) + Cl(^2P), H(^1S) CH_3(X^2A_2") and C_2H_5(X^2A): Rate Constants and Products at 293 K

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The NCO radical plays an important role in combustion processes. It is the intermediary radical species between fuel fixed nitrogen compounds and their ultimate conversion to NO_X pollutants. It is also the intermediary radical species in the formation of NO_X in the Fenimore or prompt NO_X formation mechanism. NCO chemistry also plays an important role in several NO_X abatement strategies based on the addition of various chemical additives such as cyanuric acid or urea to flue gases. As well, the NCO radical has interesting electronic properties being a linear $^2\Pi$ radical subject to the Renner-Teller effect. In spite of its chemical importance and uniqueness, there is not a great deal of information about its chemistry especially the reaction of NCO with other transient species. The reaction between NCO and a reactive species was initiated by 248 nm laser photolysis of ClNCO. The alkyl radicals were generated by the reaction of Cl atoms with H_2, CH_4, or C_2H_6, generating the radical and HCl. The reactions were carried at a pressure of 3 to 6 Torr and a temperature of 293 K. Time-resolved infrared absorption spectroscopy was used to follow the temporal dependence of the concentrations of multiple species in each reaction system, except for the NCO + Cl system where only NCO was detected. An important aspect of studying radical-radical reactions is the necessity of somehow determining the concentration of two transient species. In the present work, either multiple transients were monitored or a stoichiometric relationship between two initial transients was assumed. The infrared absorption cross sections for determining the concentrations of NCO, HNCO and C_2H_6 were measured in separate experiments. Other absorption cross sections were determined from available literature line strength data. The rate constant and product channels were determined by comparing model predictions of the temporal dependence of multiple species with the experimental observations. Rate constants were determined by minimizing the sum of the residuals between the predicted and experimental concentration profiles. Depending on the system, the following species were monitored: NCO, HCl, NH(v=0,1), HCN, HNC, HNCO, CH_3, C_2H_4 and C_2H_6. A unique feature of these results is the rapid rate constants with which all these reactions proceed. The high signal-to-noise and multiple species detection provide stringent criteria for the determination of rate constants and product channels.

B3. A Method for Time-resolved Detection of $O(^1D)$ Atoms in the Visible Enabling Simultaneous Determination of Overall Rate Constants and the Fractional $O(^3P)$ Yield

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Electronically-excited singlet oxygen, $O(^1D)$, is known to undergo both fast chemical reactions and quenching to ground-state $O(^3P)$, often by the same co-reactant. [1] Many studies of $O(^1D)$ reactivity have been motivated by its importance in the earth's atmosphere. Here, precise knowledge of the ratio of chemical reaction to quenching over the range of atmospheric N_2 : O_2 : H_2O concentration ratios and temperatures is crucial for determination of precise OH levels. [2]

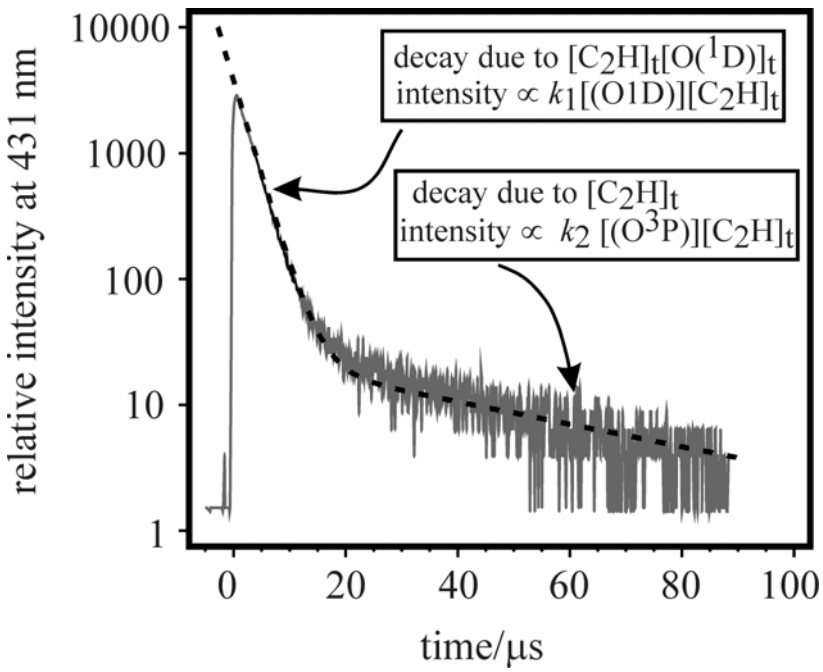
Several methods have been used over the years to monitor $O(^1D)$ in kinetic studies: VUV absorption, weak forbidden emission at 680 nm, REMPI, and chemical conversion. For these methods, determination of the fraction of $O(^1D)$ converted to $O(^3P)$ requires separate determination of $[O(^3P)]$, sometimes using a separate experimental setups. Here we present a very sensitive time-resolved technique for following $O(^1D)$ reactions which not only allows simultaneous detection of $O(^3P)$ but yields a single decay profile that gives information on both the overall removal rate of $O(^1D)$ and on the fraction of $O(^3P)$ formed.

The method is based on the chemiluminescence reaction $C_2H + O(^3P) \rightarrow CH(A) + CO$ that is known as a major source of blue emission, at 431 nm, in many hydrocarbon flames. We have recently demonstrated that the $C_2H + O(^1D)$, reaction also yields CH(A), but at a 3.5 to 5 times higher rate over the temperature range 300 - 800 K. Thus if C_2H radicals are present simultaneously with either $O(^3P)$ or $O(^1D)$, electronically-excited CH(A) is created which rapidly returns to the ground state via emission at ca. 431 nm. This 431-nm emission can therefore be employed to monitor $O(^1D)$, $O(^3P)$ and C_2H.

Generation of C_2H is straightforward using pulsed 193 nm photolysis of C_2H_2. $O(^1D)$ may also be generated using the same wavelength from, for example, N_2O. Following their simultaneous generation, $O(^1D)$ and C_2H will both react with the precursor molecules C_2H_2 and N_2O and with any added reagent. The chemiluminescence of CH(A) that is formed via $C_2H + O(^1D)$ (or via $C_2H + O(^3P)$) is proportional to the product $[C_2H]_t[O(^1D)]_t$ (or $[C_2H]_t[O(^3P)]_t$). Simultaneous presence of $O(^3P)$ and $O(^1D)$ leads to the general expression for the time-resolved intensity profile, $I_{em} \propto (k_1[O(^1D)]_t + k_2[O^3P]_t)[C_2H]_t$. Where the ratio of rate coefficients k_1/k_2 for CH(A) formation from $C_2H+ O(^1D)$ and $C_2H+O(^3P)$ has already determined in this laboratory.

If the initial $O(^3P)$ concentration is negligible, the intensity decay profile may be visually divided into a short-time domain during which the term $k_1[C_2H]_t[O(^1D]_t$ dominates and a long-time domain, when $[O(^1D)]$ is negligible, during which the term $[C_2H]_t[O(^3P)]_t$ dominates. In practice, the rate of loss of C_2H far exceeds that of $O(^3P)$ (but not that of $O(^1D)$). Thus at long times the emission profile follows $[C_2H]_t$. This information can be used to extract the rate of $O(^1D)$ removal. Back extrapolation of both the long- and short-time profiles to $t = 0$ and using k_1/k_2 gives the fraction of $O(^3P)$. In practice, the decay profiles are fitted to extract both the $O(^1D)$ removal rate and the fraction of $O(^3P)$ produced. The figure below shows a typical intensity decay profile at 431 nm under conditions in which $O(^1D)$ is removed mainly by N_2O.

From this and similar emission profiles we derive the fraction of $O(^3P)$ formed during the $O(^1D)$ + N_2O reaction as 0.037 ± 0.007, in excellent agreement with the most recent determination of this parameter of 0.04 ± 0.02. [3] We have also determined the absolute rate constant for C_2H_2 + $O(^1D)$ at room temperature as (3.2 ± 0.3) x 10^{-10} cm^3 s^{-1} with a fractional $O(^3P)$ yield of less than 0.06. Our initial measurements on the $O(^1D)$ + He reaction yields a rate constant of (2 ± 1) x 10^{-15} cm^3 s^{-1}, the precision of which is currently being improved. The sensitivity for $O(^1D)$ using this method depends on the concentration of C_2H generated, and hence on the pulsed 193 nm laser fluence. At our highest sensitivities so far we estimate our detection limit (3σ noise) for $O(^1D)$ to be 6 x 10^8 cm^{-3}, which compares very favorably with other techniques.



Typical CH(A-X) intensity decay profile at 431 nm showing $O(^1D)$ and C_2H removal mainly by N_2O. The intensity over the first *ca.* 15 μs is due to the reaction C_2H + $O(^1D)$ → CH(A) + CO. After 25 μs the concentration of $O(^1D)$ is negligible, but both C_2H and $O(^3P)$ remain, giving rise to emission via the C_2H + $O(^3P)$ → CH(A) + CO reaction. The dotted line represents the best fit associated with a fractional $O(^3P)$ yield of 0.037 from the $O(^1D)$ + N_2O reaction.

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[1] In some cases production of $O(^3P)$ occurs also as a result of chemical reaction.

[2] E. J. Dunlea and A. R. Ravishankara, *Phys. Chem. Chem. Phys*. **6** (2004) 3333 and references therein.

[3] S. Nishida, K. Takahashi,Y. Matsumi, N. Taniguchi, and S. Hayashida, *J. Phys. Chem. A*, **108** (2004) 2451.

B4. Probing Elementary Addition/Insertion Reactions from the Radical Intermediates to the Final Product Branching

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Many elementary bimolecular reactions important in chemical kinetic mechanisms, including the reactions of H, O and C atoms with unsaturated hydrocarbons, proceed through addition/insertion to form an energetically unstable radical intermediate. Our experiments generate a particular isomeric form of an unstable radical intermediate along a bimolecular reaction coordinate and investigate the branching between the ensuing product channels of the energized radical as a function of its internal energy under collision-less conditions. The experiments allow us to probe the elementary reaction from the radical intermediate to the competing product channels and determine the energetic barriers in both the entrance and the product channels. The results develop insight on product channel branching in such reactions and provide a key benchmark for emerging electronic structure calculations on polyatomic reactions that proceed through unstable radical intermediates.

The presentation focuses first on the C_4H_7 radical intermediates important in the reaction of H + 1,2-butadiene. The experiments use a molecular beam scattering method to disperse the unstable radical intermediates, formed from a photolytic precursor, by internal energy and then measure the energetic onset of the CH_3 + C_3H_4 and H + C_4H_6 product channels. Tunable VUV ionization of the products dispersed by their velocities allows us to determine how the branching to each product channel changes with internal energy in the radical even when the photolytic step produces radicals with a broad range of internal energies. The measured energetic onset of each product channel is compared to the predictions of electronic structure theories at various levels, providing a key benchmark for predictions of transition state energies in radical systems. The results also allow a critical evaluation of the Arrhenius parameters and product branching used for these elementary reactions in mechanisms proposed for 1,2-butadiene pyrolysis.

Time permitting, we also describe our recent results on the $CH_3O + CO \rightarrow CH_3 + CO_2$ reaction, which proceeds through a CH_3OCO intermediate analogous to the HOCO intermediate of the OH + CO reaction, and the CH + acetylene reaction, which proceeds through a propargyl radical intermediate. The experiments, done in collaboration with Jim Lin at Taiwan's NSRRC, probe the entrance and exit channels of the bimolecular reaction and allow us to distinguish between the very different theoretical predictions of the important exit barriers and product channel branching. Finally, we describe velocity map imaging studies to probe a key radical intermediate proposed for the reaction of O atoms with propargyl radicals.