

Final Report on Research Conducted under Grant DE-FG02-98ER14857

Work in the Carpenter laboratory under the aegis of grant DE-FG02-98ER14857 concerned the formation, properties, and reactions of organic free radicals known or believed to be important in hydrocarbon combustion. Both computational and experimental methods were employed in these studies. The results will be grouped by chemical type rather than chronologically, since the chemical classification allows a more coherent picture of the entire research project to be seen.

Formation of Radicals

The formation of organic free radicals during hydrocarbon combustion occurs primarily by hydrogen-atom abstraction, with OH being among the most important agents for this reaction. With complex organic molecules being the constituents of typical fuels, there obviously exists the possibility for hydrogen abstractions to occur at a number of sites within one molecule, leading to a variety of isomeric radicals, each of which would have its own subsequent manifold of chemical reactions. Identifying the principal sites of hydrogen abstraction is consequently an important step in understanding combustion chemistry. It has commonly been assumed that this task reduces simply to a matter of measuring (or calculating) C–H bond-dissociation enthalpies (BDEs), since it seems self evident that the highest rate constant for hydrogen abstraction should occur at the site where the breaking C–H bond is weakest. However, in studies conducted in collaboration with the Borden and Mayer groups at the University of Washington, we showed that this simple prescription is not reliable. For example, the C–H bond in methanol is 8.5 kcal/mol weaker than the O–H bond, and yet in gas-phase reactions with methyl and phenyl radicals, abstraction occurs exclusively at the O–H site. Similarly, by high-level *ab initio* calculation, we showed that degenerate $X-H + X^{\bullet} \rightarrow X^{\bullet} + X-H$ reactions occur with barrier heights that are essentially uncorrelated with the X–H BDE.ⁱ The calculations revealed several factors that can confound the simple BDE analysis, with X---X triplet repulsion in the configuration $X\uparrow\downarrow H \uparrow X$ being one of the most important.

In the laboratory, the preparation of free radicals, especially for time-resolved studies, is most commonly accomplished by UV photolysis of alkyl bromides, R–Br, or the corresponding iodides, R–I. It is a well-understood principle of physical organic chemistry that radicals, unlike carbocations, are largely resistant to unimolecular rearrangement. It has therefore seemed a safe assumption that the radical generated by R–X photolysis will have the same carbon skeleton as R in the starting material. However, in studies conducted in collaboration with Paul Houston's group at Cornell, we showed that this assumption needs to be treated with caution. Iodine-atom imaging studies conducted after photolysis of cyclopropyl iodide revealed that the dissociation occurs with concomitant isomerization of the cyclopropane.ⁱⁱ This could not be caused by ring opening of vibrationally hot cyclopropyl radicals, because the exothermicity of the isomerization showed up in excess translational energy of the iodine atoms. Calculations revealed that the photochemistry occurs with a double surface crossing. The Franck-Condon region is on an open-shell $^1(n, \sigma^*)$ surface. However, in the process of C–I dissociation, the system encounters a conical intersection with a closed-shell $R^+ I^-$ surface. Cyclopropyl cation has no barrier to ring opening, and so it is on this surface that the

isomerization occurs. But then, insidiously, the system encounters a second conical intersection that returns it to the radical-pair surface, which corresponds to the ground state at large R----I distances. Thus, while it is true that the radical has a high barrier to isomerization,ⁱⁱⁱ as physical-organic lore would lead one to expect, this double surface crossing provides a covert way for isomerization to occur on an ion-pair surface. Importantly, the same kind of surface crossing can be anticipated for many other alkyl halide photolyses, and so the untested assumption of structural integrity for the alkyl radicals produced in such processes is not generally warranted.

Properties of Radicals

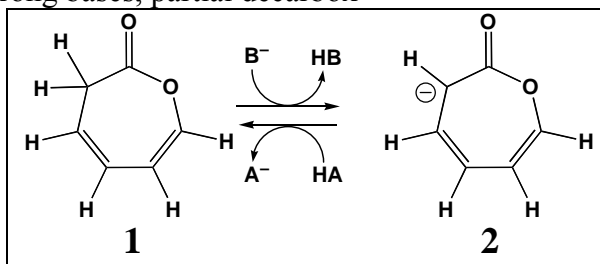
As part of the study on alkyl iodide photolysis, described in the previous section, we carried out high-level calculations on the stereochemistry and barrier for the ring opening of cyclopropyl radical.³ This work inspired direct-dynamics simulations by the Hase group, showing that the ring opening encounters a valley-ridge inflection point along the reaction coordinate.^{iv}

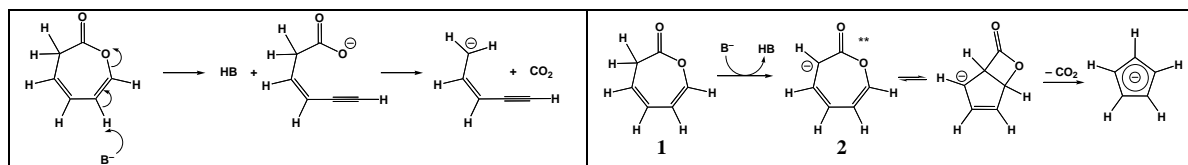
In collaboration with the Ellison group at the University of Colorado, we studied the product of cyclopropyl radical ring opening – the allyl radical. Allyl is known to be an important intermediate in combustion, and so detailed cataloging of its properties is desirable. With the Ellison group we prepared a number of isotopic derivatives that, following polarized infrared spectroscopy on the matrix-isolated radical, permitted a full empirical force field for the radical to be developed.^v

We proposed that the 2-oxepinoxy radical could be an important, and possibly detectable, intermediate in the phenyl + O₂ reaction. It is calculated to be the thermodynamically most stable C₆H₅O₂ intermediate in our mechanism, and to face substantial barriers to all unimolecular reactions that have so far been investigated. We embarked on a program to test the theoretical predictions by determining experimental heats of formation and spectroscopic signatures for the radical.

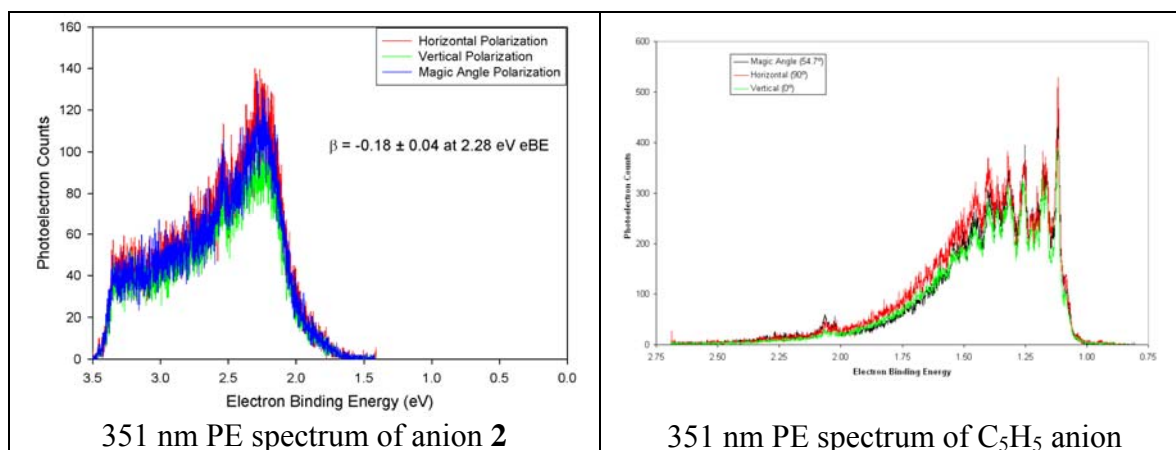
We synthesized 2(3H)-oxepinone (**1**) and, in collaboration with the group of Christopher Hadad at The Ohio State University, determined its gas-phase acidity in a flowing afterglow. The result was $\Delta_{298}H_{\text{acid}} = 352 \pm 2$ kcal/mol,^{vi} which agrees well with the B3LYP/aug-cc-pVTZ value of 349.2 kcal/mol. The anion, **2**, appears to be stable when generated in near-thermoneutral conditions, since acidity measurements determined by both forward (deprotonation of **1**) and reverse (reprotonation of **2**) reactions afford the same value. However, when **1** was deprotonated with strong bases, partial decarbox-

ylation was observed. Two plausible mechanisms were considered for this process. One was that stronger bases opened up an *E*₂-elimination channel. The other was that the excess internal energy of **2** arising from exothermic deprotonation allowed it to surmount a barrier for unimolecular decarboxylation. DFT calculations suggested that the rate-limiting barriers to these two mechanisms differ by only 2 kcal/mol, which was within the uncertainty of the calculations.

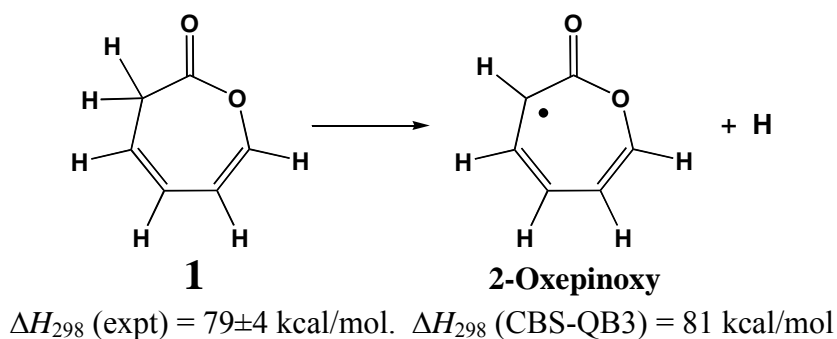




In collaboration with the group of Carl Lineberger at the University of Colorado in Boulder, we determined the UV photoelectron spectra of both anion **2** and the $C_5H_5^-$ ion produced by its decarboxylation. Both spectra are shown below. Because anion **2** is calculated to be nonplanar, whereas the radical – 2-oxepinoxy– is found to be flat, we anticipated that the (0,0) transition in the photoelectron spectrum could be hard to identify, and that turned out to be the case. Provisionally, the IP of anion **2** seems to be about 1.6 eV. With the provisional value, the combined data from the photodetachment and gas-phase acidity measurements would give the C–H bond dissociation enthalpy for **1** (in its conversion to 2-oxepinoxy + H) a value of 79 kcal/mol. CBS-QB3 calculations put this value at 81 kcal/mol.



The photoelectron spectrum of the $C_5H_5^-$ ion shows that it is definitely not cyclopentadienide, whose spectrum is well known and which has been extensively studied in the Lineberger group. This fact rules out the second of the decarboxylation mechanisms shown above. The (*Z*)-pentenynyl anion that would be generated by the first decarboxylation mechanism has not been previously prepared, and so its photoelectron spectrum is unknown.



Reactions of Radicals

The entry of the Carpenter group into the DOE-BES combustion program was initiated by our computational prediction of new mechanisms for the reaction of vinyl and phenyl radicals with O₂.^{vii,viii} Briefly, we argued that the unimolecular reactions of the initially formed vinylperoxy and phenylperoxy radicals would occur preferentially via three-membered-ring intermediates, rather than the four-membered-ring intermediates that had been proposed previously. It was the new phenylperoxy chemistry that led to the 2-oxepinoxy radical just described.

Some experimental support for our proposed vinyl + O₂ mechanism came from a collaboration with the group of Mingfei Zhou at Fudan University.^{ix} Vinyl radical was prepared by microwave discharge in ethylene, and then co-condensed with O₂ in a solid argon matrix. Formation of the vinylperoxy radical was confirmed by comparison of observed and calculated IR bands for the parent and various isotopic analogs. Visible-light irradiation of the trapped vinylperoxy radical produced a hydrogen bonded complex, H₂C–O–H----CO, which calculations revealed to be most probably formed by H-atom transfer between the pair H₂C=O H–CO, whose formation had been predicted by our mechanism.

During experimental studies on the phenyl + O₂ reaction, we discovered a hitherto unrecognized chemistry of unsaturated peroxy radicals. We found that phenyl + O₂ in benzene gave so-called benzene oxide – the product of epoxidation of benzene. When the reaction was run with C₆H₅• and O₂ in C₆D₆, the product was found to be fully deuterium labeled, showing that this was not only a formal, but an *actual* epoxidation of benzene.^x To our knowledge, the only previous examples of such chemistry had been enzyme-catalyzed. Follow-up computational work elucidated the properties of peroxy radicals that would be necessary for them to be good epoxidizing agents, and identified NC–OO• as a potentially better candidate than phenylperoxy. The possibility of O-atom transfer from peroxy radicals to unsaturated hydrocarbons should now be investigated as a new pathway in combustion chemistry.

During the final year of this grant, Steve Kroner, a graduate student from the Carpenter group, completed his Ph.D. at Cornell in the group of Prof. H.F. Davis. During this time, Kroner primarily focused on developing molecular beam sources of free radicals relevant to combustion. The sources employed photolysis or pyrolysis of stable molecules followed by supersonic expansion. Acryloyl iodide (CH₂CHCOI) was synthesized and evaluated using a Chen-type pyrolysis source as a precursor for vinyl (CH₂CH) radicals. It was found that the beam was dominated by vinyl carbonyl at lower temperatures and acetylene at higher temperatures. Beams of methyl peroxy and ethyl peroxy radicals (CH₃O₂ and C₂H₅O₂) were produced by photolysis of methyl and ethyl iodide in the presence of molecular oxygen. These beams were characterized by VUV photoionization and electron impact ionization spectroscopy. In agreement with recent studies by E. Bernstein's group (Colorado State) and Dave Osborn's group (Sandia), VUV photoionization just above threshold leads to a strong parent ion peak in the case of CH₃O₂, whereas C₂H₅O₂ undergoes essentially complete fragmentation. In addition, several different experimental configurations for production of fast photolytic H atom beams suitable for experimental studies of the H + O₂ → OH + O reaction were developed and evaluated.

A New Direction

In our last DOE-BES-supported paper, the Carpenter group initiated a new study,^{xi} which has subsequently been picked up for support by the Leverhulme Trust in the UK, and has led to additional research.^{xii} The work concerns efforts to link the known photochemical reduction of CO₂ and oxidation of water via the sacrificial redox agents (shown generically as XH₂ and Y) used in this chemistry. The overall concept can be illustrated with the following three photochemical reactions, any or all of which might involve a photocatalyst, although none is shown explicitly:



Reactions (1) and (2) represent the known chemistry. The idea is to link them by one or more additional reactions (e.g. 3), such that the sum of the individual steps gives the net transformation (4):



If successful, such a strategy would permit photosynthesis-like chemistry without the need for sophisticated molecular engineering. In particular, the separation of the difficult reduction and oxidation steps in reactions (1) and (2) means that these transformations could be carried out under mutually incompatible conditions, if that should prove advantageous. For example, the CO₂ reduction could be conducted in an anhydrous medium, which would obviously be impossible if the water oxidation had to be accomplished at the same time.

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