

K1. *Invited*: Some Observations of Vibrational Relaxation, Unimolecular Dissociation, and Unimolecular Incubation at High Temperatures

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This review is concerned with fast processes observed in shock waves, mainly through use of the laser-schlieren technique which is briefly described.

A short history of vibrational relaxation measurements leads a description of several unusual and unexpected results on such relaxation: observation of extremely fast relaxation of methyl hydrocarbons, non-linear relaxation of large, 'stiff' molecules, and the rare detection of a "double" relaxation in 1,1,1-trifluoroethane and ethane. The latter is interpreted as a consequence of slow IVR in these species.

Large-molecule dissociation and unimolecular falloff are exemplified by the reaction of norbornene, neopentane, 1,1,1-trifluoroethane, isobutene and ethane. Unimolecular incubation is exemplified with norbornene, neopentane and isobutene.

Non-RRKM falloff is observed in the fast HF elimination from 1,1,1-trifluoroethane at high temperature. The interpretation of this as a consequence of slow IVR is presented and some calculations and other suggestions as to the origin of this effect are offered.

K2. $\text{CF}_3\text{CH}_3 \longrightarrow \text{HF} + \text{CF}_2\text{CH}_2$: A non-RRKM Reaction Due to Slow IVR?

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Recently, Kiefer et al.¹ (KKSST) reported schlieren shock tube experiments on the title reaction in which they measured vibrational relaxation, incubation, and unimolecular rate constants. They noted two unusual features in the data: the steady-state unimolecular rate constants showed much less pressure variation than predicted by RRKM Theory and the vibrational relaxation exhibited two time constants. To explain their results, they invoked a breakdown of RRKM theory due to slow intramolecular vibrational energy redistribution (IVR), probably associated with the internal rotor in 1,1,1-trifluoroethane (TFE).

Breakdowns of RRKM Theory are relatively rare for thermal activation reactions with high barriers.^{2,3} Moreover, RRKM Theory is the current standard against which virtually all unimolecular (and recombination) reaction rate data are assessed. Since there is so much reliance on the accuracy of RRKM Theory, it is important to determine whether the theory has failed for this reaction, or whether there is some other explanation of the data.

Our approach is based on the MultiWell 1-D master equation code^{4,5} to simulate the KKSST shock experiments as well as the other thermal activation⁶⁻⁹ and chemical activation¹⁰ measurements on TFE. We used the RRKM model described by KKSST, which is in good agreement with the models described by Holmes et al.¹¹ Using this conventional master equation approach, we have found that the $k_{\text{uni}}(T, M)$ data reported by KKSST at 15 Torr, 35 Torr, and 100 Torr are generally consistent with RRKM Theory, but the data at 350 Torr and 550 Torr are not. We are also able to show that a conventional 1-D master equation can mimic vibrational relaxation with two time constants, although a state-to-state kinetic model will be needed^{1,12} for accurate modeling.

To test for the effects of slow IVR, the development version¹³ of MultiWell was modified to include the IVR transmission coefficient and the Leitner-Wolynes theory¹⁴⁻¹⁸ of IVR rate constants. Among other successes,^{19,20} this theory predicts¹⁷ the experimental data for trans-stilbene isomerization under conditions ranging from collision-free molecular beams at ~ 0 K to ~ 100 bar methane collider gas at 350 K.

Slow IVR, of course, exists in every molecule at sufficiently low energy, where the states are sparse and the density of resonances is too low for energy to flow freely on the energy shell. Under these conditions, a state-to-state kinetic model is needed for accurate simulations. Above the threshold for onset of IVR, a quasicontinuum of vibrational states exists and statistical models like RRKM Theory may become applicable. According to IVR theories,^{14,17,21} the reaction rate constant is modified by a transmission coefficient that accounts for the influence of finite energy flow rates during the course of reaction.

Calculations were carried out on TFE to determine the threshold energy for the onset of IVR and the IVR transmission coefficient as a function of energy. Tests were carried out with and without including collision-induced IVR, which is an important contributor in the trans-stilbene system.^{17,21-23} Tests were also carried out with an arbitrary ceiling being placed on the IVR rate constant, limiting it to rates $\leq 2\nu_{\text{ave}}$, the average vibration frequency in TFE. In all of these cases, the calculated IVR rates are so fast that IVR does not limit the reaction significantly. Similar simulations of the chemical activation data¹⁰ lead to the same conclusion.

We then carried out tests with the assumption that $k(E)$ is predicted by the Leitner-Wolynes IVR theory (but assuming collision-induced IVR is negligible), but cannot exceed a maximum *ad hoc* value $k_{\text{max}}(E) = 10^7 \text{ s}^{-1}$. Although we cannot provide a plausible physical rationale for this model, this simulation agrees reasonably well with the KKSST data.

Thus we conclude that according to the Leitner-Wolynes IVR theory, limited or slow IVR is not the reason for the discrepancy between the KKSST data and RRKM Theory. It is possible to fit the KKSST data using *ad hoc* assumptions, but no plausible physical model provides a quantitative explanation. At this time, only the KKSST data at the two highest pressures are inconsistent with RRKM theory. A thorough analysis of the experimental errors would seem to be in order.

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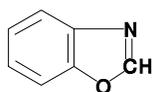
K3. Thermal Reactions of the Benzoxazole-isoxazole Family of Molecules. Experimental Results and Quantum Chemical Calculations

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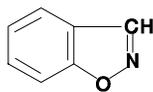
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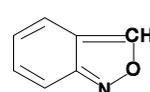
Benzoxazole, benzisoxazole and anthranil are three isomers of a molecule where a five membered ring containing both nitrogen and oxygen is fused to a benzene ring. The three isomers differ from one another by the location of the nitrogen and the oxygen atoms with respect to the benzene ring and with respect to one another.



Benzoxazole

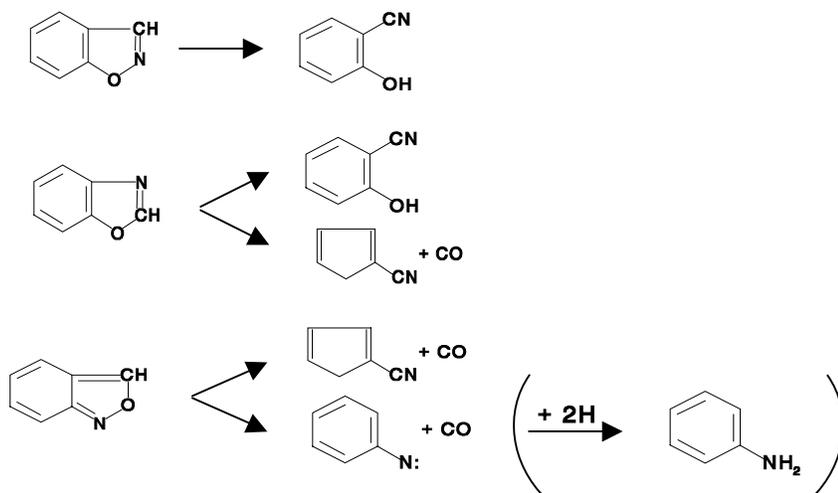


Benzisoxazole



Anthranil

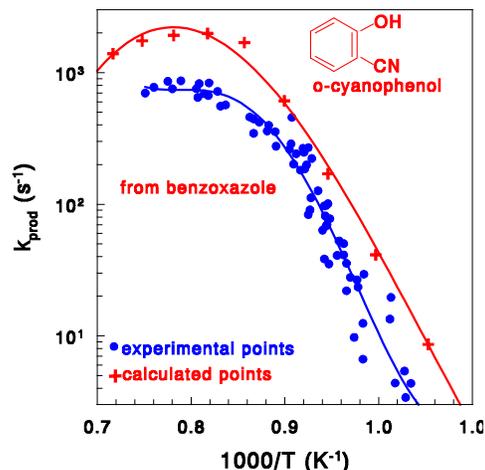
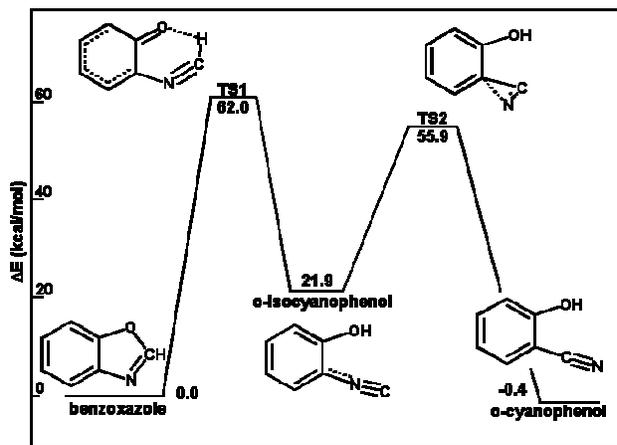
In both benzisoxazole and anthranil the nitrogen and oxygen are bound by a weak bond, whereas in oxazole these two atoms are separated by one carbon atom with relatively strong C–O and C=N bonds. When these three isomers are subjected to high temperatures, cleavage of the N–O bond in benzisoxazole and in anthranil and the C–O bond in benzoxazole takes place. Cleavage of these bonds followed by further rearrangements (and CO elimination) produces the following reaction products:



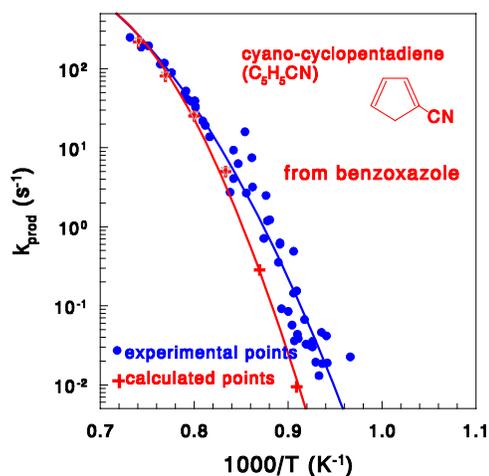
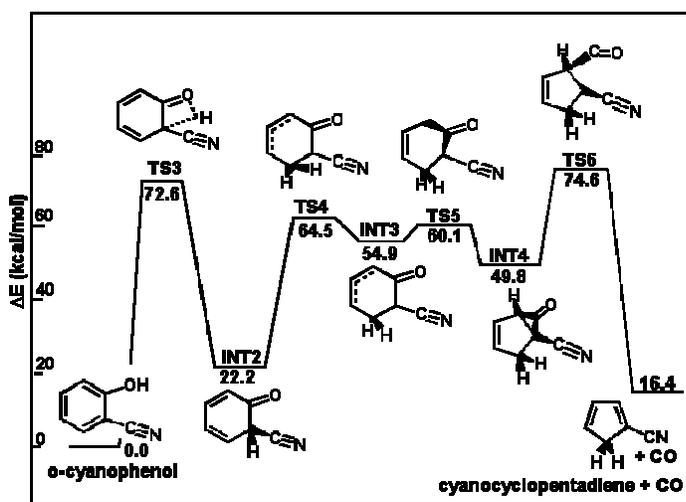
We have carried out quantum chemical calculations to evaluate unimolecular rate constants for the production of the various products and to compare the results of the calculations to experimental data obtained from single pulse shock tube experiments.

The quantum chemical calculations were performed using QCISD(T)//B3LYP/cc-pVDZ method and basis set. In view of the complexity of most of the potential surfaces, we have carried out multi well modeling for the rate constant determination, taking into account both the forward and the back reactions.

The following figures show experimental results, potential energy surfaces and the results of quantum chemical calculations for the two main products of benzoxazole decomposition: o-cyanophenol and cyano-cyclopentadiene. (Bending of the lines at high



temperatures is due to further decomposition of the products.) As can be seen, the agreement between the experimental results and the calculations are quite good.



The lower PES shows that cyano-cyclopentadiene is produced from the product o-cyanophenol rather than benzoxazole itself, its concentration is thus considerably lower. The decomposition of benzoxazole takes place at considerably higher temperatures than those of both benzisoxazole and anthranil. This is an outcome of the fact that the N–O bond in benzisoxazole and anthranil is considerably weaker than the C=N and C–O in benzoxazole.

It will be shown that the decomposition of anthranil proceeds on a triplet PES with a very minor contribution from the singlet PES particularly at the low temperature end. The minimum energy singlet \leftrightarrow triplet crossing points were calculated using CASSCF(12,10)/cc-pVDZ. Two crossing points, singlet \rightarrow triplet and two triplet \rightarrow singlet were found. Benzisoxazole isomerizes by two different pathways in one the transition states are open shell singlets and in the other closed shell. Arrhenius parameters for the various processes will be given.

K4. Intermolecular Energy Transfer Between Polyatomic Molecules

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Collisional energy transfer (CET) between molecules is the mechanism by which activation/deactivation in reactive, photochemical and photophysical processes in the gas phase take place. Because of its major importance, a great deal of experimental and theoretical efforts went into exploring various facets of the subject. The major thrust of the computational studies went into exploring CET between excited polyatomic molecules and monatomic bath gases. In the present work we report collisional energy transfer quantities for polyatomic-polyatomic collisions between a) excited benzene, toluene, p-xylene, and azulene with cold benzene bath. b) Excited benzene with toluene, p-xylene, and azulene bath. In addition, we explore CET in self-collisions of the four molecules and compare our calculations with recent experimental results. A comparison is made of CET results of polyatomic-polyatomic and polyatomic-Ar collisions. We report the average vibrational, rotational, and translational energy transferred, $\langle \Delta E \rangle$, in a single collision and discuss the effect of internal rotation on CET and the identity of the gateway modes in CET and the relative role of vibrational, rotational, and translational energies in the CET process, all that as a function of temperature and excitation energy. Energy transfer probability density functions, $P(E, E')$, for the various systems are reported and the shape of the curves for various systems and initial conditions is discussed.

K5. Experimental Observation of Ring Expansion in Five-Membered Ring Systems at Elevated Temperatures

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The formation of polycyclic aromatic hydrocarbons (PAH) is typically initiated by the recombination of small radical species followed by intramolecular rearrangement. One pathway for formation of aromatic species in pyrolytic combustion environments is *via* rearrangement of five-membered ring systems, such as fulvene (5-methylenecyclopentadiene) and its derivatives, to six-membered aromatic species. In the present study, reactions of a mixture of *t*-butylcyclopentadiene (TBCP) isomers at temperatures ranging from 1000 to 1125 K and pressures from 2 to 5 bar are examined in a single-pulse shock tube. Major products from unimolecular decomposition of the reactants include isobutene, cyclopentadiene, and toluene. The three distinct isomers of TBCP, which rapidly interconvert via H-migration around the cyclopentadienyl ring, undergo different reactions under the present conditions. The symmetric 5-TBCP isomer is expected to undergo a retro-ene reaction to form isobutene and 1,3-cyclopentadiene as well as bond scission to form *t*-butyl and cyclopentadienyl radicals. Subsequent reactions of the radical products produce isobutene and cyclopentadiene in addition to smaller concentrations of radical recombination products. Due to allylic stabilization, the asymmetric 1-TBCP and 3-TBCP isomers are expected to preferentially lose a methyl radical from the *t*-butyl moiety to form 2-cyclopentadienyl-2-propyl radicals. We propose that this system undergoes fast interconversion to form all three 2-cyclopentadienyl-2-propyl radical isomers (Figure 1) in analogy to the mechanism proposed by Melius, Miller, and Evleth [2] for the H-mediated rearrangement of fulvene to form benzene. The radical site in the symmetric isomer (**I**) is then expected to attack one of the double bonds in the cyclopentadienyl ring, allowing ring expansion to occur as shown in Figure 2. Subsequent ejection of a methyl radical produces toluene. This mechanism is identical to that expected for the H-mediated rearrangement of dimethylfulvene [5-(1-methylethylidene)-1,3-cyclopentadiene]. Results of shock-tube experiments on the TBCP isomers will be presented, and generalized rate expressions will be identified. The observed rate expressions reflect both the equilibrium reactant distributions and the rates of the individual product formation channels. The present data are useful both in understanding reactions of dimethylfulvene and as a benchmark for future modeling studies.

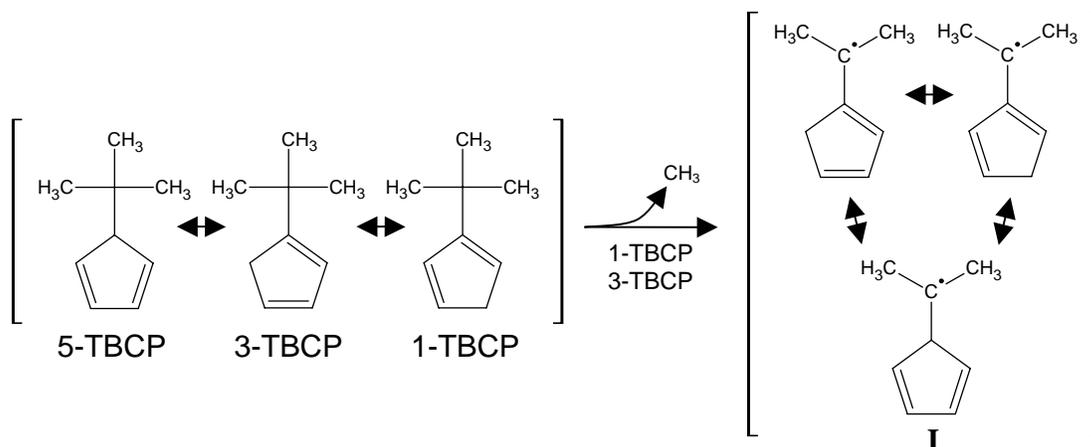


Figure 1. Precursor reactions to ring opening of *t*-butyl cyclopentadiene.

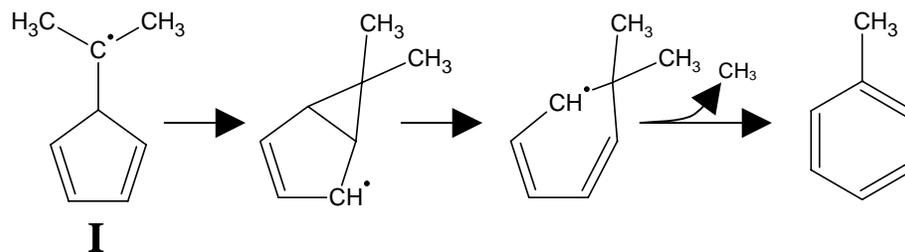


Figure 2. Ring expansion reaction of symmetric 2-cyclopentadienyl-2-propyl radical.

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K6. Experimental Investigation of the Unimolecular Thermal Decomposition of Naphthalene

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In fuel rich combustion processes, reactions of naphthalene ($C_{10}H_8$) play a dominant role in the prediction of formation and growth of polyaromatic soot precursors. The focus of the present investigation was on the unimolecular decomposition of naphthalene and the naphthyl radical at temperatures between 1350 K and 2000 K at pressures between 2 and 5 bar. The experiments were performed behind reflected shock waves at low initial concentrations of 1 – 250 ppm naphthalene and naphthyl-iodide, respectively, diluted in argon. Naphthyl-iodide as a precursor for naphthyl has been used to study the decomposition of the naphthyl radical independently from the naphthalene decay. Besides monitoring time resolved profiles of H- and I-atoms applying the highly sensitive ARAS-method, non-resonant absorption profiles of molecular products have been recorded in the wavelength regime 151 – 217 nm, too. In addition, residual GC-MS gas analysis of the post shock educts has been executed.

From H-atom ARAS profiles measured at very low initial concentrations, rate coefficients for H-elimination from naphthalene and naphthyl radical, respectively, were determined in a direct way. The results showed that the apparent activation energies of the first order rate coefficient expressions are very close to the activation energies of the unimolecular decomposition of benzene and phenyl, respectively. This is in accordance with the fact that due to the similar structure of naphthalene and benzene analogous decomposition routes may be open. The pre-exponential factor for the naphthalene decomposition is nearly one order of magnitude larger than the data from Richter and Howard [1]. For the unimolecular naphthyl decomposition, the values of the rate coefficient are about a factor of 15 smaller in the investigated temperature regime than the data from Henning's PhD-thesis [2].

The residual gas analysis from experiments with higher initial concentrations (≈ 100 ppm) revealed that besides relatively large amounts of acetylene (C_2H_2) and diacetylene (C_4H_2), tri- and tetra-acetylene (C_6H_2 and C_8H_2) are formed on a lower concentration level. Therefore, non-resonant absorption cross sections for naphthalene, acetylene and diacetylene were measured separately in the VUV and UV regime. For temperatures below 1900 K, the time dependent absorption profiles of the naphthalene molecule exhibited the same temperature dependency for the decay than the measurements of the H elimination step. Therefore, it was concluded that H elimination is the dominant initiation step of the unimolecular naphthalene decomposition.

The base model for the benzene decomposition of Wang et al. [3] which was extended by the initiation reactions measured in the present study and by a few reactions determined by our group earlier [4-5], allowed to simulate with good agreement the non-resonant VUV- and UV-absorption profiles for the whole range of the present measurements.

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