KINETICS OF COMBUSTION-RELATED PROCESSES AT HIGH TEMPERATURES

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by

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Again this year, progress is mainly reflected in publications. The following lists titles, authors, and abstracts of all publications - published, in press, or submitted-during late 1990-91.

Tunable Laser Flash Absorption: A New Technique for Measuring Rates and Yields of Chemical Reactions at High Temperatures: W.A. Von Drasek, S. Okajima, J.H. Kiefer, P.J. Ogren, and J.P. Hessler, Appl. Optics 29, 4899 (1990).

The flash absorption technique, whereby light from an excimer laser is used to measure the kinetic behavior of absorbing species in the high temperature region behind a shock front with a linear array detector, has been extended by using tunable light from a high resolution, pulsed dye laser. The use of narrowband, tunable light allows us to access isolated rovibronic transitions and, thereby, obtain state-specific kinetic information. If the oscillator strength of the transition and the absorption line profile are known, the absolute concentration may be determined. We demonstrate the technique by measuring the temporal development of the hydroxyl radical as it is formed after propane has been thermally dissociated in the presence of oxygen. We conclude that accurate kinetic measurements can be made with hydroxyl concentrations of 10^{15} cm^{-3}. This technique may also be applied to study any species which absorbs below 50,000 cm^{-1}.

High Temperature Pyrolyses of Acetylene and Diacetylene Behind Reflected Shock Waves: R. D. Kern, K. Xie, and H. Chen and J. H. Kiefer, 23rd Symposium on Combustion, the Combustion Institute, Pittsburgh, 1990, pg. 69.

A time-of-flight mass spectrometer coupled to a shock tube was used to study thermal decompositions of C_2H_2 and C_4H_2 over the temperature range 1880-2620K at total reflected shock pressures of ~ 0.4 atm. Comparison of the experimental results obtained from 3.2% C_2H_2 mixtures, one of which contained synthesized, acetone-free acetylene, and the other comprised of purified tank acetylene containing 30 ppm acetone, reveals no discernible differences in the reaction profiles. The results are modeled satisfactorily with a new 40 step reaction mechanism which incorporates a recently proposed value for $\Delta_f H^o$ (C_2H) of 130.4 kcal/mol. The concentration profiles obtained for C_2H_2, C_4H_2 and C_6H_2 are not affected by inclusion of molecular reactions in the mechanism over the temperature range covered herein. The rate employed for the dominant chain initiation at moderate temperatures, 2 $C_2H_2 \rightarrow C_4H_3 + H$, is that calculated from an RRKM analysis of new measurements on the dissociation of vinylacetylene. Strongly non-Arrhenius rate constants are employed for the crucial reaction, $C_2H + H_2 \rightarrow C_2H_2 + H$, which exceed previous estimates by more than a factor of three at 2000K. Additional support for the mechanism is provided by the kinetic data obtained from mixtures containing C_4H_2 as an initial regent. It is concluded that a fragment chain reaction mechanism is clearly dominant in the high temperature region.

Rate of the Retro-Diels-Alder Dissociation of 1,2,3,6-Tetrahydropyridine Over a Wide Temperature Range: S. S. Sidhu, J. H. Kiefer, A. Lifshitz, C. Tamburu, J. A. Walker and W. Tsang, Int. J. Chem. Kinet. 23, 215 (1991).

Rate constants for the retro-Diels-Alder dissociation of 1,2,3,6-tetrahydropyridine, to 1,3-butadiene and methanimine, have been measured over 650-1450 K. To cover this range, three separate techniques were used at three laboratories: laser schlieren and single pulse shock tube methods, and a comparative rate flow system technique. The derived rate constants are extrapolated to the high-pressure limit with an RRKM model parameterized to fit the falloff observed in the laser-schlieren measurements. The resulting high-pressure rate constants show a reduction in activation energy of about 10 kcal/mol, comparing the isoelectronic cyclohexene, but little change in A-factor. There is an apparent increase in activation energy of 4 kcal/mol over the temperature range of these experiments, which is just outside probable error. Such a rise in activation energy is in marked contrast to the drop usually seen in simple bond fission, and may reflect a change from a concerted to a stepwise, biradical mechanism at high temperatures.

The Reaction of C_4H_2 and H_2 Behind Reflected Shock Waves; R. D. Kern, K. Xie, H. Chen, and J. H. Kiefer, 18th Symposium on Shock Waves and Shock Tubes, Sendai 1991; in press.

A detailed mechanism has been employed to model successfully the homogenous pyrolysis of acetylene over a wide range of reaction conditions. Applying the model to dilute mixtures of acetone-free acetylene at high temperature produced satisfactory fits to the reaction profiles. However, the rate constant utilized for the decomposition of diacetylene, $C_4H_2 \rightarrow C_4H + H$, was that reported from an earlier study in which the total reaction pressures were considerably higher than the work of Kern et al. The rate constant for the lower pressure condition should be reduced to allow for falloff effects, but in order to model the C_4H_2 product profiles it was necessary to use the higher value.

Kiefer, et al. addressed this problem by expanding the reaction mechanism from 40 steps to 85. Significant changes included increased rates for the dissociation of C_6H_2, C_8H_2 and C_4H, the latter justified by theoretical and experimental evidence for the stability of C_4. Some key reactions of the mechanism are as follows:

$2C_2H_2 \rightarrow C_4H_3 + H$ (1)
$H + C_2H_2 \rightarrow C_2H + H_2$ (2)
$C_4H_2 \rightarrow C_4H + H$ (3)
$C_4H \rightarrow C_4 + H$ (4)
$C_6H_2 \rightarrow C_6H + H$ (5)
$C_8H_2 \rightarrow C_8H + H$ (6)
$C_4 + C_2H_2 \rightarrow C_6H + H$ (7)

Reaction (3) is the main source of degenerate branching at very high temperatures, along with lesser though significant contributions from reactions (4) - (7). The thermochemical properties of C_2H, C_4H, C_6H_2, C_6H, C_8H_2 and C_8H, the most important parameters in this mechanism, have all been re-evaluated.

These recent concepts are tested by performing dynamic mass spectrometric sampling of reflected shock zone gases containing mixtures of diacetylene and hydrogen in a neon diluent: 1% C_4H_2 - 30% H_2; 3% C_4H_2 - 75% H_2; 4% C_4H_2 - 10% H_2. The compositions were chosen to suppress the formation of solid carbon which impeded a previous study of C_4H_2 with lesser amounts of H_2. The temperature range covered for the experiments described herein is 1640 - 2110K at total pressure of ~ 0.4 atm. The product concentrations for C_2H_2, C_6H_2 and C_8H_2 depend upon the C_4H_2/H_2 ratio; C_6H_2 and C_8H_2 are completely suppressed at C_4H_2/H_2 of 1:30. Particle formation was greatly reduced except at high temperatures for C_4H_2/H_2 of 4:10. The proposed model provides acceptable fits for the experimental profiles except for those experiments which exhibited carbon atom imbalances due to solid formation.

Thermal Isomerization of Cyclopropanecarbonitrile. The Use of Multiple Chemical Thermometers in Single Pulse Shock Tube Experiments: A. Lifshitz, I. Shweiky, J.H.

Kiefer and S. S. Sidhu, 18th Symposium on Shock Waves and Shock Tubes, Sendai 1991; in press.

Tsang has shown that the use of internal standards to determine temperatures in single pulse shock tube experiments reduces considerably the scatter in the data. Shock non-idealities which may cause serious errors in the temperature calculations cancel out when an internal standard is used. The best choice of a standard for a specific study is a unimolecular reaction which proceeds with a rate comparable to that of the subject reaction. Inappropriate overlap between these two rates may require in many cases the use of more than one internal standard for a particular study. In order to examine this option three different internal standards were used in this investigation as chemical thermometers to calculate temperatures behind reflected shock waves. They were based on three chemical reactions which are known to obey a first order rate law with known Arrhenius rate parameters:

$$CH_3CHClCH_3 \rightarrow CH_3CH{=}CH_2 + HCl \qquad (1)$$

$$CH_3CH_2CH_2Cl \rightarrow CH_3CH{=}CH_2 + HCl \qquad (2)$$

$$(CH_3)_3C\text{-}OH \rightarrow (CH_3)_2C{=}CH_2 + H_2O \qquad (3)$$

The thermal isomerization of cyclopropanecarbonitrile (c-C_3H_5CN) was chosen as the test reaction in this investigation. It was studied behind reflected shocks in a pressurized driver single pulse shock tube in the temperature range 900-1050K at total densities of approximately 3×10^{-5} mol/cm^3.

The Homogeneous Pyrolysis of Acetylene II: The High Temperature Radical Chain Mechanism: J. H. Kiefer, S. S. Sidhu, R. D. Kern, K. Xie, H. Chen, and L. B. Harding, Combust. Sci. and Tech.; in press.

A comprehensive kinetic/thermochemical model for the high-temperature radical chain decomposition of acetylene and the polyacetylenes is presented. This mechanism is tested against new shock tube data: time-of-flight mass spectra in C_4H_2/H_2 mixtures over 1600-2100K and laser schlieren experiments in C_2H_2 covering 2700-3500K. Some earlier time-of-flight measurements on C_2H_2 are also modeled. The paper includes a very extensive consideration of species thermochemistry, and the model is in full accord with the current consensus, having $\Delta_f H^\circ(C_2H) = 135.5$ kcal/mol. Entropies are computed from recent determinations of molecular parameters for C_2H and from new high-level ab initio calculations for C_4H reported here. The time-of-flight measurements support $\Delta_f H^o(C_4H_2) = 111$ kcal/mol or 28.24 kcal/mol for the $[C_t - (C_t)]$ group. Rate constants for the key C-H fission reactions of the acetylenes are taken from RRKM calculations calibrated against the direct measurements of dissociation in C_2H_2 and C_4H_2. Although there are still some problems with the thermochemistry, in particular, the model probably underestimates the participation of small carbon clusters, it does accurately simulate the early kinetics of the pyrolysis quite generally. The model also resolves some long-standing problems; for example, the current high value for $\Delta_f H^o$ of C_2H is now fully compensated by an increase in its entropy, and the chosen rate of C_4H_2 dissociation is completely in line with the direct measurements of this rate.

The Importance of Hindered Rotations and Other Anharmonic Effects in the Thermal Dissociation of Small Unsaturated Molecules: Application to HCN : A.F. Wagner, J.H. Kiefer and S.S. Kumaran, 24th Symposium on Combustion; submitted.

A standard low-pressure limit RRKM rate constant is shown to significantly underestimate measured thermal dissociation rates for C_2H_2 and HCN if the correct value of the bond dissociation energy is used. An explanation for this discrepancy is sought by examining anharmonic effects, especially those involving large angle bends that lead to isomerization. For HCN, an approximate, adiabatic quantum mechanical calculation of the complete spectrum of all bound states up to the dissociation energy is performed. The spectrum is dominated at the dissociation energy by a partially hindered 2D rotation, even though the isomerization barrier on the potential energy surface exceeds 40 kcal/mole. This occurs because adiabatic influences from the two stretching frequencies reduce the effective isomerization barrier and increase the effective mass of the rotation. The anharmonic effects from this hindered rotation and its coupling with the anharmonic H stretch modify the rate constant so as to largely remove the discrepancy with experiment. It is argued that the same effects are present in the dissociation of other small unsaturated molecules such as C_2H_2.

Dissociation Rates of Propyne and Allene at High Temperatures and the Subsequent Formation of Benzene: J. H. Kiefer, P. Mudipalli, S. S. Sidhu, R. D. Kern, K. Xie, and

H. Chen, 24th Symposium on Combustion; submitted.

The thermal decompositions of allene and propyne have been studied in the shock tube using laser schlieren observation of density gradient [2 and 4% allene - Kr; 2% propyne - Kr; 1700 - 2500K; 100 - 650 Torr] and time-of-flight mass-spectrometry [3% allene - Ne; 3% allene, 5% H_2; 3% propyne; 3% propyne, 5% H_2; 1690 - 2090K; 240 - 330 Torr]. The lower concentration LS experiments provide C-H fission rates virtually independent of isomerization and secondary processes. Over 1700 - 3000K we obtain log k (cm^3/mol-s) = 16.09 - 62.3(kcal/mol)/2.3 RT for allene. The rate of propyne dissociation is slightly smaller, in close accord with its greater stability, so that the recombination rates are nearly identical for the two isomers. The TOF spectra show C_2H_2 as main product with appreciable C_4H_2, CH_4, and C_6H_6. There were no discernible effects of H_2 addition. The C_2H_2 and C_4H_2 appear to arise from chemically activated decomposition of some C_6H_6 adduct formed by C_3H_3 dimerization. Modeling of LS experiments in 4% allene at low temperatures shows that only $2C_3H_3 \rightarrow C_6H_6$ has the right kinetic behavior for benzene formation, and that the rate of this process must have a strong negative temperature dependence in essential accord with a recent QRRK analysis. This study offers the first kinetic evidence on the path to benzene in this system, as well as information on its rate.

The Formaldehyde Decomposition Chain Mechanism: E.A. Irdam, J.H. Kiefer, L.B. Harding and A.F. Wagner, Int. J. Chem. Kinet.; Submitted.

A kinetic mechanism for the chain decomposition of formaldehyde consistent with recent theoretical and experimental results is presented. This includes new calculations and measurements of the rate constant for the abstraction reaction

$$CH_2O + H \rightarrow HCO + H_2$$

The calculation uses a multi-reference configuration interaction wavefunction to construct the potential energy surface which is used in a tunnelling-corrected TST calculation of the rate constant. The rate constant for the bond fission

$$CH_2O + M \rightarrow HCO + H + M$$

at high temperatures was determined by an RRKM extrapolation of direct low temperature measurements. This mechanism has been successfully tested against laser-schlieren measurements covering the temperature range 2200 - 3200K. These measurements are insensitive to all but the above two reactions and they confirm the large, non-Arrhenius rate for the abstraction reaction derived here from theory. Modeling with the derived mechanism of previous experiments using IR emission, ARAS, and CO laser absorption, is quite satisfactory. The branching ratio of the rate of the faster molecular dissociation (CH_2O + (M) —> CO + H + (M)), to that of the bond fission reaction, was estimated to lie around 2 or 3 over 2000 to 3000 K. This ratio is consistent with recent theoretical estimates and most experimental observations.

In addition to the above, two papers are in preparation.

1. "The Pyrolysis of Silane." This is a very extensive study of the dissociation and subsequent condensation which is now complete. A full description will be attached to our next report.

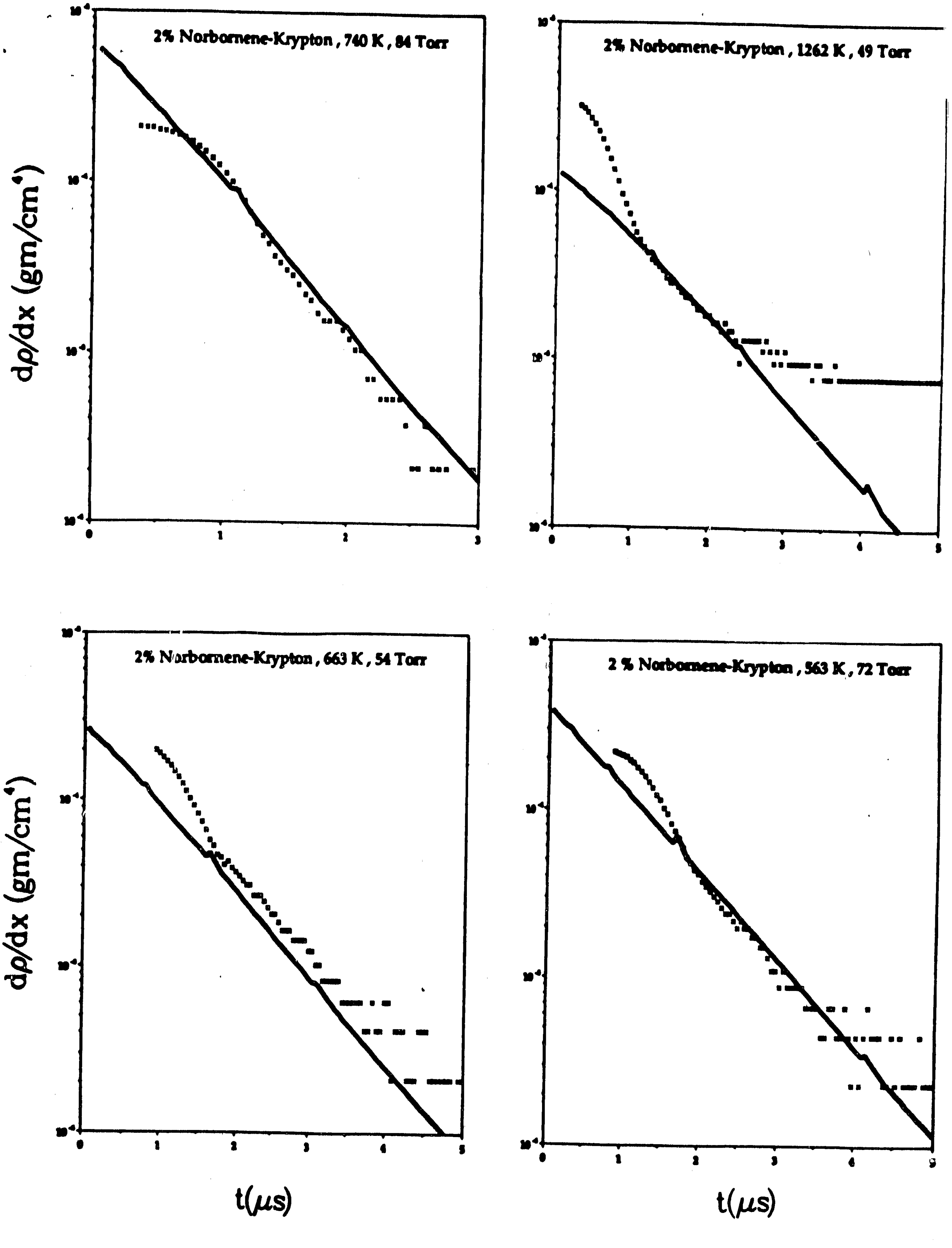
2. "The Unimolecular Dissociation of 3,4-Dihydro-2H-Pyran at High Temperatures." This study involves a collaboration with W. Tsang (NIST) which defines the retro-Diels-Alder dissociation of this large molecule over 600 -- 1500K and 12 orders of magnitude in the rate constant. This study is an extension of our investigation of unimolecular falloff in large molecules and of the temperature dependence of k_∞.

New work during the past year includes the unexpected and remarkable observation of vibrational relaxation in norbornene (C_7H_{10}) and norbornadiene (C_7H_8). This resulted from an attempt to observe falloff in norbornene dissociation by the use of extremely weak low-pressure shocks in dilute norbornene -krypton mixtures (2% C_7H_{10} - Kr). Norbornene easily dissociates by a retro-Diels-Alder process giving ethene and cyclopentadiene, but the molecule is so large that falloff is not easily discerned even for temperatures (>1200K) where dissociation is very fast.

To produce clean shock waves in dilute Kr mixtures with temperatures below 1200K and post-shock pressures as low as 30 torr, we introduced various converging-diverging (Laval) nozzles just downstream of the diaphragm. Thus the helium flow following diaphragm rupture is forced into a very narrow constriction (our greatest area reduction is a factor of 50) greatly slowing its flow and the shock velocity. With this arrangement we have been able to produce perfectly formed shocks in Kr with temperatures of 600K and pressures as low as 30 torr. There are other methods for producing weak shocks, for example using very thin diaphragms or heavy drive gases, but we have found these to give badly distorted shock waves which cannot be used for sensitive laser-schlieren measurements. Whereas an extensive series of test runs in pure Kr with our various nozzles (area reductions of 3-50 at the nozzle throat) show perfectly clean flow, i.e., no detectable beam deflections except at the shock front, over a wide range of conditions. Probably this is because high pressure bursts quickly displace the diaphragm and the remaining flow irregularities are much reduced at the nozzle throat.

A set of semilog density gradient profiles from 2% norbornene-krypton are shown in the figure. Also shown are simulations using the so-called Bethe approximation (the process is very accurately a first-order conversion of unrelaxed to relaxed.) For the relaxed enthalpy of norbornene we used the frequency assignment of Shaw, et al., J. Chem. Phys. 89, 716 (1988). The excellent agreement of the calculated and observed relaxation profiles is now decisive evidence that the process is indeed vibrational relaxation. One of these profiles, however, that at 1262K, shows a late positive deviation which is from dissociation of the norbornene. In this experiment one can see the transition from relaxation to dissociation and can estimate a dissociation induction time of ~2.5 μs (lab time) which corresponds to about 5×10^{-7} atm-s in real time.

We have also resolved the relaxation in norbornadiene where the process is even more interesting -- there is a local maximum in the gradient. It should be noted that these are the largest molecules whose vibrational relaxation has ever been seen by any technique. That we are able to resolve this relaxation to temperatures as high as 1500K means that we can obtain large-molecule unimolecular induction times, a subject of considerable theoretical interest (see for example J. Shi and J. R. Barker, Int. J. Chem. Kinet., 22, 187 (1990).). The only such induction times presently available are for diatomics, and one very rough estimate for N_2O (Dove, et al., 15th Symposium on Combustion, p. 913, 1974).


2% Norbornene-Krypton , 740 K , 84 Torr
2% Norbornene-Krypton , 1262 K , 49 Torr
2% Norbornene-Krypton , 663 K , 54 Torr
2 % Norbornene-Krypton , 563 K , 72 Torr
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