

HIGH INTENSITY INFRARED LASER IRRADIATION CALORIMETRY: DIRECT-DETERMINATION OF
HEAT INPUT TO CHLORODIFLUOROMETHANE AND ETHYL ACETATE

W. Braun, J. T. Herron, W. Tsang and K. Churney

Chemical Kinetics Division, National Bureau of Standards, Washington, D.C. 20234
(U.S.A.)

Any quantitative description of multiphoton induced decomposition of polyatomic molecules must ultimately be based on information regarding the degree of dissociation as a function of the energy absorbed. Heat measurements, as reported here, define uniquely the boundary conditions satisfying the type of distribution functions which characterize the energy disposition following laser irradiation and the subsequent molecular dissociation of a sample. It is clear that if an RRKM formulation adequately describes the dissociation of an energy rich molecule produced by laser irradiation, then if the distribution function is known for a given system, the dissociation rates can be correctly calculated, i.e., the system is completely determined as far as the unimolecular dissociation process is concerned.

The calorimeter is shown schematically in Figure 1. The central sample cell is made of copper and is gold-plated. The cell is surrounded by eight chips (thermopiles) each containing a 6 x 8 array of thermocouples for a total of 384 thermocouples. Essentially all the heat absorbed by the sample cell is transmitted through the thermopile. The temperature difference between the inner sample cell and the outer copper block is reflected in a measured emf. The sample cell is connected to a gas handling system as well as to an on-line gas chromatograph, allowing for precise heat measurement as well as analysis of the gas mixture after the laser irradiation. A typical heat pulse shown in Figure 2, consists of a rapid rise immediately after the laser pulse, subsequently followed by a much slower decay. Total conversions were, with few exceptions, kept to less than 10%. The products monitored were C_2F_4 from the decomposition of CF_2HCl ; and C_2H_4 from the decomposition of ethyl acetate.

Results of the total amount of energy deposited in the system are presented in graphical form using triangular plots in Figures 3, 4, and 6. Figures 3, 4, and 6 also show a temperature scale which defines the vibrational temperature of the system depending on the extent of equilibration. The vibrational temperature, T(K) is calculated from the following relation

$$Q_{total} = C_v(\text{at temperature } T)(T-298) - f(3/2 R) (T-298).$$

From the extent of decomposition and the calculated vibrational temperature one can calculate from the macroscopic (thermal) rate constant the residence time of the molecule in the medium i.e., the time required to account for the amount of dissociation at the specified (calculated) vibrational temperature. These are also displayed at various points on the figures.

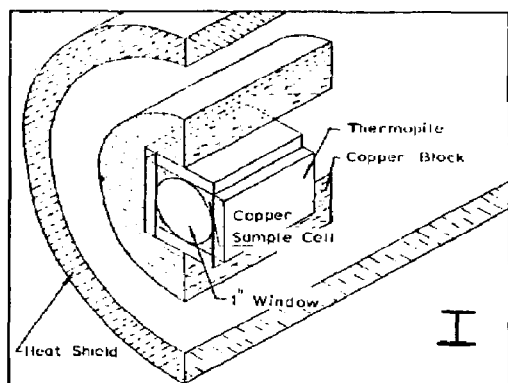


Fig. 1. Heat flow laser calorimeter. Sample cell (~ 1 in $\times 1$ in $\times 1$ in) has two ZnSe windows. Heat flows from gold-plated sample cell to copper block through 384 thermocouple junctions. End plates and collimators not shown.

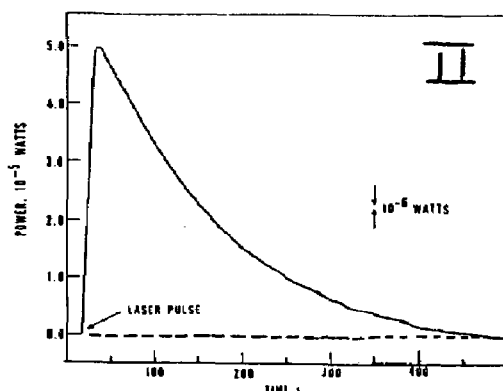


Fig. 2. Typical heat pulse following laser pulse. Energy deposited is area under the curve.

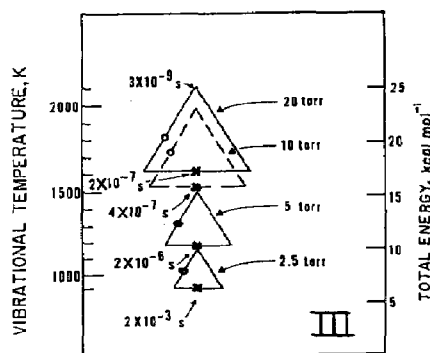


Fig. 3. Heat absorbed, calculated vibrational temperatures and reaction times for the absorption of IR radiation by neat CF_2HCl at different pressures. Points labeled as X represent system at complete equilibrium; points labeled as o represent system in vibrational and rotational equilibrium. Scale representing vibrational temperature is shown.

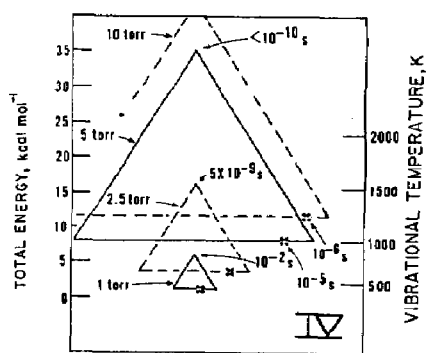


Fig. 4. Heat absorbed, calculated vibrational temperatures and reaction times for the absorption of IR radiation by CF_2HCl at different pressures with added helium (10:1). The equilibrium point, labeled X, is shifted from the center line because of the added helium.

At low pressure of CF_2HCl (2.5 torr) if all of the energy deposited by the laser resided in vibrational degrees of freedom the system would have a (vibrational) temperature of about 1200 K. The calculated reaction time would be about 2 μs . Complete equilibration would have reduced the system temperature to about 900 K and increased the reaction or residence

time to about 2×10^{-3} s, which we estimate to be too long. We assume that the temperature collapses via shock formation which occurs approximately at sonic velocities (times of the order of 1 μ s to 10 μ s). Thus this system deviates from thermal equilibrium. At the highest pressure, 20 torr, if the system were completely equilibrated during the laser pulse, the temperature would be about 1600 K and the reaction time somewhat longer than the laser pulse duration. The system under these conditions is apparently very close to or actually at complete thermal equilibrium. We arrive at a similar picture if helium is added to the CF_2HCl , Figure 4 and we look at the product yield vs. CF_2HCl pressure as shown in Figure 5.

In contrast to the CF_2HCl results, which showed definite thermal behavior at high substrate pressures, the results obtained for ethyl acetate, shown in Figure 6, indicate non-thermal behavior over the entire pressure range investigated. At the highest pressures if the system were completely thermally equilibrated, the maximum temperature would be 900 K. The reaction time calculated from this temperature is about 300 μ s, which we consider to be too long to account for the measured amount of dissociation.

If the deposited energy were to remain entirely in vibrational degrees of freedom the reaction time $\sim 10^{-4}$ s is in excess of our estimate of reasonable V-R-T relaxation times. This would suggest that the distribution function responsible for the dissociation of ethyl acetate cannot be characterized by a simple Boltzman vibrational energy distribution. Molecules possessing higher energies, near the dissociation limit, are more populated than predicted by a simple Boltzman function.

The present observations are consistent with recent results in our laboratory [1], and in others [2,3], that molecules which can dissociate via two different dissociation channels do so in a time interval considerably shorter than the laser pulse duration. Only if the calculated dissociation times are comparable to, or only slightly longer than the laser pulse duration would we expect to see a simple (single) temperature characterizing the system. The present heat measurement results on the ethyl acetate system are consistent with our postulate [4] that there is a bottleneck in the absorption process. As a result of such a bottleneck the bulk of molecules are 'cold' and a small number, those passing through the bottleneck, can become disproportionately 'hot'.

Our earlier results [5], which showed that mixed systems, allyl methyl ether or isopropyl bromide mixed with ethyl acetate, dissociated at relative rates dictated by the 'thermal' rate constant ratios, coupled with our present heat measurement results cause us to speculate that at high total pressures of these mixtures the distribution function for both species are similar, yet are not the thermal distribution functions.

References

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- (4) W. Tsang, J. A. Walker, W. Braun, and J. T. Herron, paper presented at this conference by W. Braun.
- (5) D. Gutman, W. Braun, and W. Tsang, J. Chem. Phys., 67, 4241, 1977.

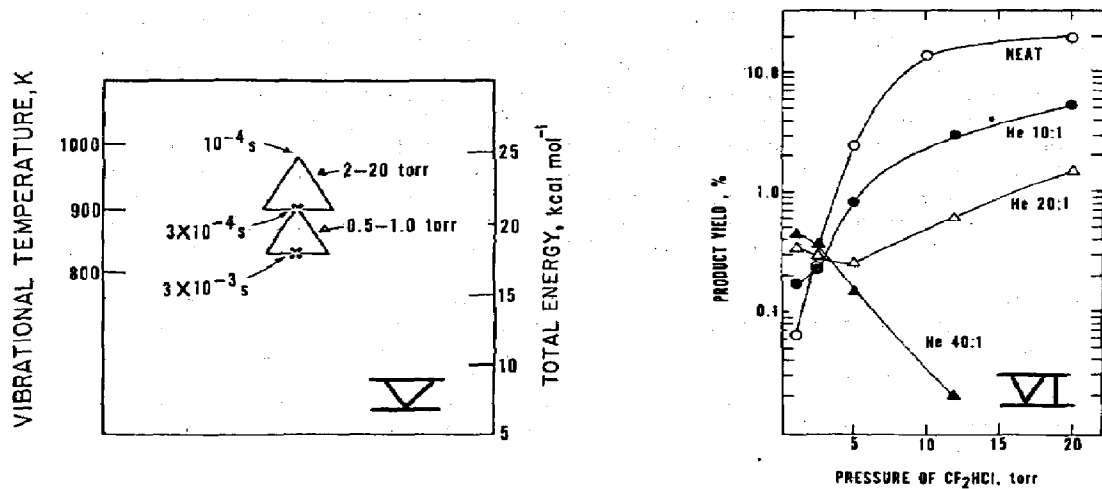


Fig. 5. Product yields in photolysis zone resulting from the absorption of IR radiation by neat CF_2HCl and CF_2HCl -helium mixtures.

Fig. 6. Heat absorbed and calculated vibrational temperatures and reaction times for the absorption of IR radiation by neat ethyl acetate.