LASER SCHLIEREN, SHOCK TUBE STUDIES OF HIGH TEMPERATURE
HYDROCARBON PYROLYSIS RATES

Progress Report

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ABSTRACT

Progress during the period has been in five areas; completion of a rigorous physical optics study of laser-schlieren measurements, completion of a study showing that angled laser beam refraction by the shock front can give accurate values for total density change, continuation of a study of the induction time for CO₂ dissociation, improvements in equipment, and near completion of an extensive study of propane pyrolysis. The propane pyrolysis study has provided rates for the primary step

over the range 1400 - 2400K.

Progress since the last report (dated March 1980) has been in five areas:

i) completion of a detailed and rigorous physical-optics analysis of the laser-schlieren technique (see attached paper 1), ii) completion of a short study of the efficacy of angled-beam refraction measurement of total density change in shock waves (see attached paper 2), iii) introduction of a microcomputer (Intertec Superbrain) for the digital analysis of recorded beam - deflection signals, and its implementation, iv) analysis of CO_2 dissociation experiments for rate, relaxation time, and induction time, and v) detailed analysis of an extensive series of experiments on the pyrolysis of propane. In addition the possibility of using a converging - diverging nozzle to reduce transverse waves in exothermic reaction has been tested. The following is a somewhat expanded discussion of these topics.

Physical Optics Analysis

We have now completed, and are publishing, a very thorough optical analysis of the differential detector signals generated by passage of a shock wave through a narrow, Gaussian laser beam. A full paper describing this is attached as paper No. 1. This paper is scheduled to appear in the January 15th issue of Applied Optics.

The motivation for the above optics study is twofold: First, many previous experiments using the laser-schlieren technique have established a very high precision of measurement. If this precision is to be fully exploited, the analysis must be as unambiguous as possible. Previous theoretical work (cited in paper No. 1) relied upon unjustified geometrical optics assumptions which improperly treated beam expansion and totally neglected diffraction. One purpose of the full physical optics study was the establishment of a rigorous connection between detector signal and density gradient which correctly defines the limits of this connection and the true magnitude of corrections necessary for rapidly varying gradients. Second, accurate location of time origin (the "instant" of process

initiation by shock compression) in schlieren signals is absolutely essential to the accurate interpretation of pyrolysis experiments. There appears to be no way to make such an assignment except through a detailed optical analysis of the beam-shock front interaction. Such an analysis is contained in paper #1 and a method for time - origin location to $\pm 0.1\text{-}0.2 \mu\text{s}$ is proposed there. This method has been used in the analysis of the CO_2 and propane pyrolysis experiments described below.

Angled Beam Refraction Measurement of Density Change

One difficulty with schlieren measurements for shock densitometry has been their inability to establish the net density change in the shock wave, either that due to shock compression or this coupled with following reactive changes. In the attached paper #2, we have used measurements of Snell's law refraction by the shock front of a narrow laser beam, this beam being set to impinge on the shock front at a shallow angle, to determine net density (refractive index) change. The results reported there for Ar and Kr establish that such density changes can be measured with high accuracy (to $\pm 1\%$).

Angled beam measurements can be a useful adjunct to normal laser-schlieren. Determination of density in the shocked gas is a check on assumed thermodynamic properties and predicted composition. The method can also be used to determine gas refractivities at high temperature which will be a necessity for aromatic pyrolysis studies such as those suggested in the attached proposal. Finally, these measurements establish in a very direct way the extremely high accuracy which can be achieved in laser-beam deflection measurement.

Apparatus Improvements

We have purchased a microcomputer (intertec "Superbrain") which is now installed in the laboratory and has been used for all the experiments described in this report. The computer is used to provide direct digital presentation (Integral Data 400 printer) and processing of the schlieren signals recorded by the Lecroy wave-form digitizers.

Implementation of this system has required extensive hardware and software development, both for the transfer of stored digital data and its processing. We now compute density gradient directly for each recorded digital voltage (one recording/50 ns) which is printed and graphed without operator intervention. Examples of output are shown below in the discussion of the propane experiments.

In addition to the above we have modified our photodiode amplifier to supply the sum of signals from the two detector halves as well as the difference. We expect the sum signal may prove useful in the assignment of time origin. A complete description of our current apparatus is given in paper #2.

CO₂ Dissociation Experiments

A series of 40 experiments in 5 and 10% CO₂ - Kr mixtures have now been performed. Our preliminary analysis (which needs further refinement) determined induction times $t_i \sim 2 \tau_{\text{relax}}$, where τ_{relax} is the vibrational relaxation time. Compared to the only previous measurements of a polyatomic dissociation induction time, those of Dove and Teitelbaum⁽¹⁾ on N₂O, these times are extremely short. Because the measured times are so short, time-origin location becomes very critical and we do not have a really reliable method for such location at the very low pressures necessary for these experiments. We are investigating a new method, however, and if this is successful we will repeat some of the CO₂ experiments. We are also investigating the theory of such induction times.

Pyrolysis of Propane

We have now completed and largely analyzed a set of 50 experiments on propane pyrolysis. These involved mixtures of 1%, 2%, and 4% propane in Kr, and were recorded using the most current apparatus including the microcomputer. A set of "typical" results is shown in Figs. 1-4. Also shown are the predicted density gradients from a simulation using the mechanism and rate constants given in the attached list labeled "Propane Mechanism". The agreement between calculated and

Propane Mechanism

No.	Reaction	Rate Constant			Reference
		A (cgs)	$n(T^{-n})$	E_a (cal/mole)	
1- C_3H_8	= $CH_3 + C_2H_5$	see text			
2- $C_3H_8 + CH_3$	= $CH_4 + i-C_3H_7$	4.5000E+12	0.0	10300	(2)
3- $C_3H_8 + CH_3$	= $CH_4 + n-C_3H_7$	1.3000E+13	0.0	10300	(2)
4- $C_3H_8 + H$	= $H_2 + i-C_3H_7$	8.0000E+13	0.0	8000	(2)
5- $C_3H_8 + H$	= $H_2 + n-C_3H_7$	2.3500E+14	0.0	8000	(2)
6- $i-C_3H_7$	= $CH_3 + C_2H_4$				(3)
7- $n-C_3H_7$	= $CH_3 + C_2H_4$				(3)
8- $i-C_3H_7$	= $H + C_3H_6$				(3)
9- $n-C_3H_7$	= $H + C_3H_6$				(3)
10- $C_2H_4 + H + M$	= $C_2H_5 + M$	1.4000E+16	0.0	0.0	(4)
11- $2CH_3 + M$	= $C_2H_6 + M$	4.4500E+31	-4.5	0.0	(4)
12- $C_2H_6 + CH_3$	= $CH_4 + C_2H_5$	5.0119E+14	0.0	21495	(5)
13- $C_2H_6 + H$	= $H_2 + C_2H_5$	1.3183E+14	0.0	9383	(6)
14- $C_2H_5 + H$	= $CH_3 + CH_3$	3.7154E+13	0.0	0.0	(6)
15- $C_2H_5 + H$	= $H_2 + C_2H_4$	1.3962E+12	0.0	0.0	(6)
16- $CH_4 + M$	= $CH_3 + H + M$	4.6774E+17	0.0	93148	(7)
17- $CH_4 + H$	= $CH_3 + H_2$	7.2444E+14	0.0	15047	(7)
18- $C_2H_4 + M$	= $H_2 + C_2H_2 + M$	2.0893E+17	0.0	79032	(8)
19- $C_2H_4 + M$	= $H + C_2H_3 + M$	2.5704E+17	0.0	96491	(8)
20- $C_2H_4 + H$	= $H_2 + C_2H_3$	6.9172E+14	0.0	14498	(8)
21- $C_2H_3 + M$	= $H + C_2H_2 + M$	7.9435E+14	0.0	31479	(9)
22- $C_2H_3 + H$	= $H_2 + C_2H_2$	1.0000E+13	0.0	0.0	(4)
23- $H_2 + M$	= $H + H + M$	3.6308E+12	0.5	92527	(10)

predicted gradients is generally very good except for the combination of long times and high temperatures. For short times, at all temperatures, the gradient is only sensitive to the rates of reactions (1) $C_3H_8 \rightarrow CH_3 + C_2H_5$ and (10) $C_2H_5 + M \rightarrow H + C_2H_4 + M$, as is illustrated by the presentation of the gradient due to each separate reaction in Fig. 4. (The total or observed gradient is a simple algebraic sum of the gradients from each reaction in the mechanism⁽¹¹⁾). Since the ethyl radical (C_2H_5) concentration is pseudo-steady in $<1\mu\text{sec}$ (the initial rise in Figs. 2 and 3 is a consequence of the increase of C_2H_5 to steady concentration), for all later times the rate of (10) is coupled to that of (1). Then the thermochemistry and gradient are that of $C_3H_8 \rightarrow CH_3 + C_2H_4 + H$, at the rate of (1). Thus, although the high temperature examples show deviations at long times, these are a consequence of inadequacies in the mechanism which have no effect on the derivation of a rate for reaction (1). We have accordingly determined rates for reaction (1) which are shown in Fig. 5. Here each experiment is matched with an optimum choice for k_1 for that experiment. It should be noted that the constraints imposed by this kind of data on k_1 are very sharp. An incorrect choice changes both magnitude and slope, too high a value giving too steep a slope through a rapid temperature drop (and conversely) as is illustrated in Fig. 6. Thus, to provide a complete fit both the magnitude and temperature dependence of k_1 , as well as the rates for important secondary reactions in the early stages (essentially 3-9), must be completely sound. Theoretical consideration of the results of Fig. 5, including possible fall-off effects, is underway.

The inadequacy of the listed mechanism at later times and high temperature is primarily a difficulty with the ethene reactions (18) - (22), as is shown by the individual reaction gradients of Fig. 4. We have been unable to obtain a good fit to all of our high temperature data from a single set of rates for these reactions. The rate constants given here are literature values (reactions (18),

(19), (20)⁽⁸⁾ and estimates ((21) and (22) ⁽⁹⁾ (4)). It is not clear which of this large set should be regarded as solid, so there are too many variables for any simple systematic variation procedure. In the attached proposal we suggest additional experiments which should assist in resolving this problem.

Although we still have some difficulties with the later stages of the pyrolysis reaction, these problems have little effect on the determination of the primary rate, that of reaction (1). These experiments then greatly extend the temperature range over which this rate has been measured and do this with good precision. The experiments also offer the possibility of determining rates for several of the later secondary reactions which are considerable importance in oxidation and sooting.

Finally, in an attempt to suppress transverse wave structure generated by exothermic reaction, we have test fired weakly detonable propane - oxygen - rare gas mixtures with a converging - diverging nozzle positioned just before the test section. In the absence of the nozzle these mixtures gave accelerating shock waves with quite violently pseudo-oscillatory schlieren records. With the nozzle attention of the shock speed was observed but the violent oscillations persisted. This experiment was not a success.

1. J.E. Dove, W.S. Nip, H. Teitelbaum, 15th Symposium (International) on Combustion, (Combustion Institute), 1974) p. 903.
2. These rates have been selected as 5 times those suggested by C-C. Chiang and G.B. Skinner, 18th (International) Symposium on Combustion (to be published), on the basis of fit to our low temperature C_3H_8 data.
3. A. Lifshitz, J. Phys. Chem. 79, 686 (1975). The Lifshitz rates for reactions (6) - (9) were modified (reduced) for unimolecular falloff. The propyl radicals remain steady-state nevertheless, and the results are thus insensitive to these rates.
4. D.B. Olson, T. Tanzawa, and W.C. Gardiner, Jr., Int. J. Chem. Kin., 11, (1979).
5. P.D. Pacey and J.H. Purnell, J. Chem. Soc. Faraday I, 68, 1462 (1972).
6. P. Camilleri, R.M. Marshall, and J.H. Purnell, J. Chem. Soc. Faraday I, 70, 1434 (1974).
7. P. Roth and T. Just, Ber. Bunsenges. Phys. Chem., 79, 682 (1975).
8. T. Just, P. Tott, and R. Damm, in 16th (International) Symposium on Combustion (The Combustion Institute, 1977) p. 961.
9. S.W. Benson and G.R. Haugen, J. Phys. Chem, 71, 1735 (1967).
10. A.L. Myerson and W.S. Watt, J. Chem. Phys., 49, 245 (1968).
11. J.H. Kiefer, "The Laser-Schlieren Technique in Shock Tube Kinetics", Chapter in "Shock Tubes in Chemistry", A. Lifshitz Ed., to be published by Marcel Dekker, N.Y.

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FIGURE CAPTIONS

Fig. 1. Experimental density gradients (x) in gm/cm^4 , and computer simulation (-) using the listed mechanism, for a shock in 1 C_3H_8 - 99Kr. For the first eight points, the shock front is still crossing the beam, and these points do not indicate bulk-gas, reactive gradient. The temperature and pressure shown refer to post-shock frozen reaction conditions.

Fig. 2. Experimental (x) and computed (-) gradients for a shock in 2 C_3H_8 - 98Kr. (c.f. Fig. 1. caption).

Fig. 3. Experimental (x) and computed (-) gradients for a shock in 4 C_3H_8 - 96Kr. (c.f. Fig. 1. caption).

Fig. 4. Experimental (x) and computed (-) gradients for a high - temperature shock in 4 C_3H_8 - 96Kr. Here individual computed reaction gradients are shown. These are identified as follows:

★ ★	Reaction (22)
△ △	(10)
○ ○	(1)
× ×	(11)
◇ ◇	(18)
* *	(21)

The gradient for reactions (11) and (22) is negative (exothermic reaction), the absolute value being shown. At late times both the computed and experimental total gradients are also negative. Again the absolute value is plotted. The sudden downward "spike" in gradient indicates the point of transition to negative values. Those reactions not shown have $d\rho/dx < 10^{-7} \text{ gm/cm}^4$. (c.f. Fig. 1. caption).

Fig. 5. Normalized rates $r/(\text{C}_3\text{H}_8)$ in s^{-1} for the reaction

as derived from the present experiments. The experiments group quite closely into two pressure-ranges: i) 170-257 Torr (0), and ii) 395-475 Torr (x); the slight separation of these two groups then indicates the presence

of some falloff. The solid line shows the results of Skinner⁽²⁾ which he presumed were near the high-pressure limit.

Fig. 6. The experiment of Fig. 1 repeated with a computed gradient using twice the "optimum" rate for reaction (1). Comparison with Fig. 1, which does use this optimum rate, illustrates the strong effect on both magnitude and slope of such an alteration.

Fig. 1

Fig. 2

Fig.3

Fig. 4

Fig. 5 .

Fig. 6

Fig. 3