

Boundary Layer Effects on Pyrolysis Behind Reflected Shock Waves in Narrow Tubes

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Introduction

In some experiments on the thermal decomposition of propane in a flow system at temperatures between 1100°K and 1400°K, the usual difficulty was experienced in evaluating the role of surface reactions in the chain decomposition. To try to avoid this difficulty, further experiments were performed using a small diameter, low-pressure shock tube with helium as the driver gas, and employing the reflected shock wave technique to heat a propane-argon mixture to calculated temperatures in the range 1800°K to 2260°K. A study of the products and the dependence of extent of decomposition on calculated temperature behind the reflected shock wave revealed strong evidence of non-ideal behavior, undoubtedly related to Duff's [1] observations of the marked effects on the main stream of boundary layer development behind the incident shock wave. Measurement of the distance between contact surface and incident shock confirmed the conclusions drawn from the chemical evidence: that in narrow low-pressure shock tubes the loss of gas from the hot flow region behind the incident shock to the boundary layer is appreciable, and only part of the reactant gas is heated to high temperature by the reflected shock wave.

Experimental

The goal was to study the decomposition of C¹³-labelled propane; since only a small amount was available, a small (25 mm i.d.) low-pressure shock tube was employed. Reaction temperatures in the neighborhood of 2000°K were obtained behind the reflected shock wave. The low-pressure section, 120 cm long, was of standard-wall Pyrex tubing selected for uniformity of bore. The brass driver section was 61 cm long. Diaphragms (one-mil cellophane) were punctured by a solenoid-driven needle.

Helium at an initial pressure of 1.3 atm was used as the driver gas in all experiments. The ambient temperature was 300 ± 2°K. Initial pressures of the reactant gas mixture in the low-pressure section ranged from 3.3 to 7.5 mm Hg depending on the desired shock strength. This mixture contained in all cases 90.0 mole per cent argon (Matheson research grade) and 10.0 mole per cent propane. Gas chromatographic analyses confirmed the absence of significant impurities in these gases. Vacuum handling of reactants and products was adequate to avoid introduction of impurities exceeding one mole per cent of the initial propane in any given experiment.

Incident shock wave speeds were determined from oscillograms which displayed timing marks at 10 μ sec intervals together with signals from three shock wave detectors located 75, 95, and 115 cm from the diaphragm. The detectors were thin-film nickel oxide resistors which have been described elsewhere [2].

These measurements indicated that shock wave attenuation was negligible, less than one per cent in 20 cm of travel. It appeared that small discrepancies (7 or 8 per cent)

between observed velocities and those calculated from the initial pressures could be adequately explained by assuming that slight flow obstructions resulted from incomplete diaphragm removal. Measurements made with a detector in the end plate showed that the high-temperature dwell time after the shock was reflected was one m sec or greater.

Products were collected for analysis by pumping the entire contents of the shock tube through two traps in series, both cooled with liquid nitrogen. The first, a 4-loop reentrant trap, collected condensables; the second contained Linde Molecular Sieve 5A to retain methane and argon. Condensables were determined quantitatively by gas chromatography, using a thermal conductivity detector calibrated separately for each product of interest.

Calculations

Using the usual one-dimensional shock wave theory, conditions behind the incident and reflected shock waves were computed from the observed incident shock wave speeds. Calculations were made assuming unreacted gas in internal thermal equilibrium at high temperature. Enthalpy data for propane below 1500°K were taken from published tables [3], and values at higher temperatures were computed on the basis of Pitzer's vibrational assignment [4] and Pitzer and Gwinn's treatment of hindered rotation [5].

Since ideal one-dimensional shock tube behavior was not realized in these experiments, these calculations should not be taken very seriously. The calculated reflected shock temperatures are presented here only to provide a rough indication of experimental conditions. The observed incident shock wave speeds and the calculated reflected shock temperatures in three experiments are listed at the top of the table.

Results of Three Experiments on Decomposition of
Propane by the Reflected Shock Wave Technique

	Run 1	Run 2	Run 3
Shock wave speed (incident)	1.12 mm/ μ sec	1.19 mm/ μ sec	1.31 mm/ μ sec
Calculated T behind reflected shock	1800°K	1960°K	2260°K
Propane (initial)	0.581 cm ³	0.414	0.255
Propane (final)	.283	.204	.127
Fraction decomposed	.513	.507	.502
Products			
Ethane	.029	.014	.006
Ethylene	.197	.142	.077
Acetylene	.019	.031	.041
Propylene	.036	.015	.004

Results and Discussion

Since incident shock wave attenuation was negligible in preliminary experiments, serious departures from one-dimensional flow were first suspected when attempts were made to understand the product analyses. Referring to the table, one sees some apparent discrepancies. On the one hand, the conversion of propane is only 50 per cent and is virtually independent of incident shock speed and calculated reaction temperature in the three experiments. On the other hand, that the reaction temperature is actually increasing with increasing shock strength is fairly obvious from the trend in product distribution, showing acetylene increasing at the expense of other products as calculated temperature goes up.

It is difficult to reconcile these observations and to explain the surprisingly low extent of decomposition if ideal shock tube behavior is assumed.

Considering first the low conversion of propane to products: one can estimate a minimum rate of decomposition by assuming that propane disappears by first-order unimolecular dissociation to ethyl and methyl radicals, with an activation energy of 85 kcal (rather a high estimate) and a frequency factor of $2 \times 10^{13} \text{ sec}^{-1}$. The half-life of propane with these assumptions, leaving out all consideration of chain reactions, would be less than 10^{-4} sec at 2000°K . In our experiments, the minimum available reaction time at the high temperature (one m sec or greater) amounts to at least ten half-lives even using this unrealistically low estimate of rate. The conclusion is almost inescapable that only about half the propane is heated to the calculated reaction temperature.

If this is so, the results obtained can be viewed as follows: It is as if the reactant gas were divided into two parts, one of which is restricted to sufficiently low temperatures that little pyrolysis occurs, while the other is decomposed to high conversion. The two portions are then mixed (by the sampling procedure) and the apparent per cent conversion is determined by analysis of the mixture. The measured extent of decomposition would thus be governed by the original division of the sample.

A mechanism to explain qualitatively these results can be devised starting from Duff's observations [1]. From his report of the close pursuit of the incident shock wave by the contact surface we infer that main stream-boundary layer interactions impose a severe limitation on the quantity of gas that can exist in the intervening hot flow region. The influence of the boundary layer on the main stream is not simply encroachment of the former on the latter; in addition there is an actual flow toward the wall of gas in the main stream. The reactant gas thus tends to concentrate near the wall where some of it is bypassed by the central core of cold driver gas before the reflected shock wave arrives.

In our experiments, reaction occurs only behind the reflected shock; hence only that portion of reactant gas that remains in the hot flow region until it is traversed by the reflected shock will undergo decomposition at a rate characteristic of the calculated reflected shock temperature. That which has been lost to the boundary layer behind the incident shock may undergo little or no decomposition on passage of the reflected shock wave.

In order to estimate in another way the importance of such effects in the present experiments, some additional runs were made, with conditions as in Run 2 of the table, but with the third detector (115 cm station) mounted in midstream to permit measurement of the time between arrival of the incident shock and the contact surface at this station. The results varied from run to run, but the observed time interval never exceeded one-half the value given by one-dimensional theory. It was evident that a significant fraction of the reactant gas had been lost from the hot flow region.

In another experiment gas was sampled from near the center of the end plate, where by the above mechanism the apparent conversion of propane should be high. A small sample bulb with stopcock was attached to the end plate; with the stopcock open the diaphragm was burst, and then the stopcock was closed. The condensable part of the sample recovered from the bulb contained 27 mole per cent propane; that from the rest of the shock tube contained 63 mole per cent unreacted propane. Again, marked loss of gas from the hot flow region was indicated.

Conclusions

This investigation presents rather extreme examples of difficulties which are introduced by boundary layer effects. It is difficult to estimate the extent to which one must go, either by employing a tube of larger diameter or by working at higher pressure, in order to reduce below a tolerable limit the loss of reactant gas from the hot flow region. The obvious desirability of avoiding dynamical similarity with these experiments indicates that an answer cannot be obtained by simple dimensional analysis.

However, the very fact that extreme cases are presented should give some insight into the direction in which interpretation of experiments can err when boundary layer effects are ignored. For example, it is not difficult to see how an illusory indication of low activation energy for decomposition could result if an unsuspected fraction (not too strongly dependent on shock strength) of the reactant gas were lost from the hot flow region.

The observed variations from run to run of the duration of hot flow can introduce other experimental complications as well. These variations presumably result in part from the finite but ill-defined rate of diaphragm rupture.

In conclusion, it is important to emphasize that none of the effects reported here would have been suspected on the basis of the shock wave velocity measurements, which gave no clear indication of incident shock attenuation or unusual disagreement between calculated and observed incident shock velocities. From the available evidence we must conclude that shock wave velocity measurements do not provide a reliable criterion for appraising the importance of departures from uniform flow in the hot gas when small, low-pressure shock tubes are employed. Even with larger tubes, especially if activation energies are to be derived from the data, independent measurements should probably be made to determine whether loss of reactant gas to the boundary layer is significant.

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References

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