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Correction for Finite Quenching Rates in Shock-Induced Methane Pyrolysis

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Theme

IN this study, the feasibility of using a simple shock tube, without modifications to enhance the quenching rate, is explored. Such a simple shock tube is used to study the pyrolysis of methane as a step in studying reaction rates of hydrocarbons in processes involving combustion and formation of air pollutants. The shock tube was operated in the tailored interface mode, and the reaction temperature ranged from 1,650 to 2,100 K, with a total reaction pressure up to 6.4×10^5 Pascal.The chemical reaction occurred behind the reflected shock wave, near the end wall of the test section. A sampling system was developed to allow a sample of product gas to be withdrawn from the test section before it was contaminated by the driver gas. A correction for finite quenching rate was developed and applied in this study as well as an error analysis.

Contents

The driven section of the shock tube was a rectangular-shaped aluminum duct 8.54 m long. The inside dimensions were 7.62×15.22 cm. The driver section was a cylindrical tube 1.83 m long with an inside diameter of 17.8 cm. Further details of this shock tube are included in Ref. 1.

The rate constants for the methane pyrolysis reaction reported in the literature differ from one another significantly.[2-6] The most recent study[6] of this reaction in the shock tube was accomplished using optical methods to follow the progress of the reaction. The rate constant from that study is nearly an order of magnitude smaller than that reported in earlier studies in which the direct sampling of the reaction products was used. To summarize the results known to data on the pyrolysis of methane, it is clear that the reaction follows first-order kinetics with an apparent activation energy of $398 \pm 42 \times 10^{-3}$ J/mol (95 ± 10 kcal/mol) and a frequency factor of $2.5 \pm 1 \times 10^{13}$. There does appear to be some pressure effect on the reaction rate, although there is not complete agreement on the extent. A satisfactory reaction mechanism has yet to be established, particularly at temperatures below 2,100 K.

Sampling System: The progress of reactions studies in this investigation followed by extracting from the shock tube a quenched sample of the reaction gas mixture at a certain time and analyzing it by means of a gas chromotograph to determine its composition. The sampling system to accomplish this consisted of a stainless steel probe, solenoid valve, and sample cylinder mounted on the end wall of the shock tube. The stainless-steel sample cylinder had a volume of 250 cm^3. In these experiments the probe was flush with the end wall of the shock tube. The inside diameter of the probe and piping was 0.76 cm. Before a test run the sample cylinder was filled with pure argon at the testing pressure. After a run the sample cylinder was pressurized with nitrogen to a convenient working pressure.

Reaction Quenching and Dwell Time: In shock tube chemical kinetics studies, it is important that the test gas not react at temperature T_2 (behind incident shock) but then react rapidly at temperature T_5 (behind reflected shock) to obtain a sample of product gas large enough for chemical analysis. In this study T_2 ranged from 800 to 1000 K. In this range, the pyrolysis of methane is negligible, as shown by the previously reported literature results. Temperature T_5 varied from 1,650 to 2,100 K. The reaction conditions of Region 5 are eventually destroyed by the rarefaction wave reflected from the end of the driver. For chemical kinetics studies it is important that this rarefaction wave cool the reaction mixture rapidly enough to freeze the chemical composition. This sudden cooling also causes the time in which the reaction mixture is exposed to the conditions of Region 5 (the reaction dwell time, t_a) to be well-defined. A measure of dwell time was obtained from a photographic trace of the pressure transducer output. In these experiments, the cooling rate was also determined from the pressure trace. The measured dwell time and the composition of the frozen reaction mixture allow the determination of the rate constant of the reaction.

Determination of the Rate Constant: Since the pyrolysis of methane has been firmly established as a first-order reaction,[2-6] only the density ratio of methane in the test gas before and after reaction is needed. With the first-order kinetics and the reaction dwell time obtained from the pressure traces, the rate constant is given by

$$k = [\ln(\rho_0/\rho)]/t_a \qquad (1)$$

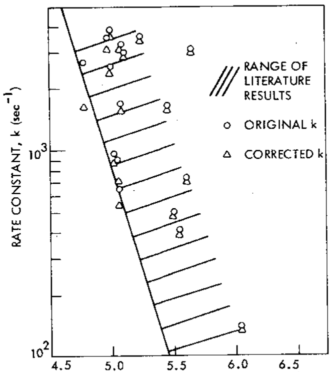

Fig. 1 Effect of finite quenching correction on rate constant.

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Here t_a is the time during which the uniform conditions of Region 5 persist.

A sample of the original methane-argon mixture was analyzed in each run and served as the calibration gas for the gas chromatograph. The sample volume and calibration volume were equal. However, the methane concentration varied widely from one sample to another, and it was found that the relationship between chromatograph peak area and concentration was not linear over the entire concentration range. Consequently, a calibration curve of the chromatograph integrated detector output as a function of the mole fraction of methane in the injected gas was made to determine the response of the detector over a range of concentrations. From this calibration, the ratio of methane concentration in the product gas to that in the reactant gas was found to be

$$(C/C_0)_{\mathrm{CH}_4} = \exp[2.303(A_x - A_c)/m] \tag{2}$$

where A_x and A_c refer to the methane peak areas given by the integrated detector response of the chromatograph to the product and reactant gases, respectively, and m is the slope of the calibration line. In the final calculation of the concentration ratio of methane before and after reaction, it was necessary to take into account the dilution of the reacted gas with nitrogen and the fact that the sample cylinder originally was filled with pure argon. Corrections for these items applied to the concentration ratio given by Eq. (2) yield the following density ratio from which the reaction rate can be determined in Eq. (1).

$$\left(\frac{\rho}{\rho_0}\right)_{\mathrm{CH}_4} = \left(\frac{C}{C_0}\right)_{\mathrm{CH}_4}\left(\frac{P_N}{P_f - P_I}\right) \tag{3}$$

where P_I is the initial pressure before sampling, P_f the pressure immediately after sampling, and P_N the pressure after the sample cylinder is pressurized with nitrogen.

Figure 1 shows the logarithm of k plotted as function of the reciprocal temperature. Included in this figure is a line representing the data of Hartig et al.[6] for temperatures from 1850 to 2500 K. The comparison is good in this temperature range (especially at 2000 K) as well as to temperatures as low as 1650 K.

Pressure Effect: The experimental data was obtained over a range of pressures with the intent of determining what effect pressure has on the rate constant for the pyrolysis of methane. Using an uncertainty in T_5 and P_5 of 4%, runs that fall within these ranges of particular values of T_5 and P_5 were grouped together, and the average values were calculated. The results shown in Table 1 indicate a definite a pressure dependence. From this data it is apparent that the reaction rate increases with both temperature and pressure.

Quenching Rate Correction: The quenching rate in these experiments was estimated from the end wall pressure trace. Assuming the quenching occurs isentropically, the rate of temperature change is related to the pressure change by

$$\frac{dT}{dt} = \frac{\gamma - 1}{\gamma}\left(\frac{T_0}{P_0}\right)\left(\frac{P}{P_0}\right)^{-1/\gamma}\frac{dP}{dt} \tag{4}$$

which is obtained by implicitly differentiating the isentropic P-T relationship with respect to time. The initial state, T_0 and P_0, is taken to be State 5 and dP/dt is estimated from the slope of the end wall pressure trace. In this way the quenching rate was found to be 10^5K/sec.

Since this quenching rate is somewhat less than that reported in the literature where enhancement (single pulse shock tube) of the rarefaction wave has been used, the effect of a finite cooling rate on the computed rate process was explored analytically. The governing equation for the rate process is $dC(t)/dt + k(t)C(t) = 0$. Ideally, the temperature during the reaction should remain constant at T_5 for some time t_a and then instantaneously drop to a value at which chemical reaction is negligible. In the present situation from t_a to t_b, the temperature decreases isentropically at some finite rate dT/dt until at time t_b the temperature is sufficiently low so that reaction ceases. The Arrhenius activation energy is assumed to be constant over the temperature range considered. The solution of the differential equation is then

$$-\ln\left(\frac{C}{C_0}\right) = kt_a + \int_{t_a}^{t_b} \exp[-E_a/RT(t)]\,dt \tag{5}$$

The assumption that a finite cooling rate has negligible effect on the rate constant is equivalent to neglecting the integral term on the right-hand side of Eq. (5). This can lead to differences of several percent in resulting values of the calculated rate constants.

Table 1 Pressure effect on reaction rate (k)

Average T (K)	Average P (pascal)	Average k (sec $^{-1}$)
2000	3.91×10^5	2.02 (10^3)
	6.10×10^5	2.61 (10^3)
1800	5.01×10^5	0.53 (10^3)
	6.13×10^5	1.62 (10^3)

The integral in Eq. (5) has to be evaluated numerically because of the form of the temperature function $T(t)$. This function is obtained by evaluating the derivative dT/dt in Eq. (4) at various points in the time interval $[t_a, t_b]$. Linear regression was used to fit a straight line to these values of the derivative, thus obtaining an equation of the form $dT/dt = \alpha t + \beta$. Integration of this equation then yields a quadratic temperature function for use in Eq. (5). Typical values of t_a and t_b are 2 and 7 m/sec, respectively. Using the "best" literature value[6] for E_a of 4.02×10^5 J/mol (9.6×10^4 cal/mol), the integral was evaluated for the data of this study. By taking into account the value of this integral, a new rate constant was calculated. The new rate constant, evaluated at the experimental temperatures, is included in Fig. 1. Figure 1 graphically compares the original and the corrected values of the rate constant. The effect of correcting for this finite quenching rate is to make the values of the rate constant of this study fall closer to the "best" literature line.

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