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Production of major reaction products in the initial steps of the thermal decomposition of naphthalene. Experimental shock-tube results and computer simulation

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Abstract

Initial steps in the thermal decomposition of naphthalene were studied behind reflected shocks in a pressurized driver single pulse shock tube over the temperature range 1350–1650 K and densities of $\sim 3 \times 10^{-5}$ mol/cm^3. The present manuscript concentrates on the initial steps in the decomposition of naphthalene, rather than its function in producing molecules having more rings toward the formation of PAH etc. For the purpose of studying the low extent of decomposition, relatively low temperatures were used where the extent of reaction is small so as to prevent a secondary or higher generation of reactions that might obscure the initial decomposition process to take place.

Five major decomposition products that were found in the post shock mixtures of naphthalene were acetylene, di-acetylene, benzene, phenyl acetylene, and acenaphthylene. Products that did not exceed 1% at their highest concentration were not considered both in the product distribution map as well as in the computer simulation. These were methane, ethylene, allene + propyne, methyl naphthalene, and indene. Indene, with somewhat higher than 1% at its maximum, could not be computer simulated with reasonable agreement. The total disappearance rate of naphthalene, in terms of a first-order rate constant is given by $k_{\text{total}} = 7.33 \times 10^{13} \exp(-364/RT)\ \text{s}^{-1}$ where R is expressed in units of kJ/(K mol). A concise kinetics scheme containing 15 species and 19 elementary reactions accounts for the observed major decomposition products with reasonable agreement. The kinetics scheme, as well as results of the computer simulation and the sensitivity analysis are shown.

Keywords: Naphthalene; Decomposition; Shock wave; Simulation

1. Introduction

There are several basic reactions that naphthalene undergoes where the active species are naphthyl radicals. In most cases the initial reactant is naphthyl iodide. This is owing to the relatively

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low C–I bond dissociation energy that is ~272 kJ/mol [1], as compared to the much stronger C–H bond in naphthalene (~469 kJ/mol) [1]. The reactions of naphthyl radicals with both ethylene [2] and acetylene [3,4] have been thoroughly investigated both experimentally, by computer simulation and by evaluating potential energy surfaces using quantum chemical methods. In these studies three membered rings were obtained, in somewhat different mechanisms, resulting in the isomerization of the formed naphthyl acetylene to acenaphthylene [2–4]. The isomerization of azulene to naphthalene was also studied in a single pulse shock tube [5] and by other methods [6]. Shock induced pyrolysis of naphthalene and several other aromatics towards the formation of a large number of PAH with different structures and number of aromatic rings was investigated, suggesting general mechanisms but without detailed kinetics scheme [7,8]. Wang and Frenklach have published a very thorough investigation calculating a large number of rate parameters for reactions that are related to the formation of PAH starting from benzene via naphthalene [9]. Most of the rate constants were evaluated by quantum chemical calculation of the relevant potential energy surfaces [10].

There have been also studies on the oxidation of naphthalene and its derivatives by several groups of investigators [11,12]. Pitch [13] and Dagaut [14] have composed a detailed kinetics scheme with many elementary steps for the ignition and oxidation of α-methyl naphthalene. Lindstedt et al. have studied the kinetics and thermodynamic issues in the formation and oxidation of aromatic species [15].

Similar to the initiation step in benzene, the step in naphthalene decomposition is an H-atom ejection from the ring. This behavior is owing to the fact that the C–H bonds, both in benzene and in naphthalene (~469 kJ/mol) [1] are considerably weaker than those of the C–C bonds (~565 kJ/mol) [1]. In view of the complete symmetry of benzene there is only one initiation channel with reaction coordinate degeneracy of 6. In naphthalene there are two channels producing α-naphthyl and β-naphthyl radicals. In each of these initiation reactions, the degeneracy of the reaction coordinate is 4. The pre-exponential factor for the ejection of H-atom from benzene is thus higher than that for each channel in naphthalene by about 1.5. Also, the activation energies for the H-atom ejection processes are by some 30 kJ/mol lower than the ΔH^0 of the reaction. This is probably owing to a slight slide from the first order limit at the high temperatures involved.

The participation of naphthalene in reactions where products of several aromatic rings are formed is an important contribution to the formation of PAH. However, as mentioned, the present article will not deal with the latter, it will examine only the initial steps in the decomposition of naphthalene and in the production of major reaction products. These products contribute to the formation of PAH.

2. Experimental

The decomposition of naphthalene was studied behind reflected shocks in a pressurized driver, 52 mm i.d. single-pulse shock tube. The tube, made of electro polished stainless steel tubing, as well as all the transfer tubes, were heated and maintained at 110 °C with an accuracy of ±2 °C. The driver section had a variable length up to a maximum of 2.7 m and could be varied in small steps in order to obtain the best cooling conditions. A 36 liter dump tank was connected to the driven section at 45° angle near the diaphragm holder in order to prevent reflection of transmitted shocks that can travel back and forth and reheat the reaction mixture. The driven section was separated from the driver by "Mylar" polyester film of various thicknesses depending upon the desired shock strength. Dwell times of approximately 2 ms were measured with high frequency miniature pressure transducers with an accuracy of ~5% and cooling rates were approximately 5×10^{-5} K/s.

Reaction mixtures containing 0.3% naphthalene diluted in argon were prepared manometrically and stored in 12 L glass bulbs at 700 Torr. The vapor pressure of naphthalene at 110 °C is around 28 Torr. Both the bulbs and the gas manifold were pumped down to ~10^{-5} Torr before the preparation of the mixtures. Naphthalene was obtained from Aldrich Chemical Co. and was listed as 99% pure. Chromatograms of unshocked samples did not show any products that appeared in the shocked samples.

After running an experiment, samples were transferred from the downstream end of the

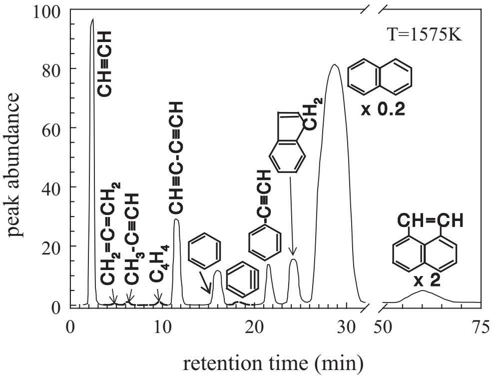

Fig. 1. Chromatogram of the major reaction products of shock heated 0.3% naphthalene in argon to 1575 K.

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