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Laser Powered Homogeneous Pyrolysis of 1,3-Butadiene

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Radical kinetics and energetics at elevated temperatures continue to be vexing problems even after many years of study. Heterogeneous reactions, harsh conditions, complex product distributions and species with only transient lifetimes all contribute to make free radical kinetics difficult to study under many chemically interesting conditions. Laser Powered Homogeneous Pyrolysis (LPHP) affords the opportunity to alleviate a number of these difficulties[1,2], allowing new insight into free radical kinetics to be obtained. LPHP avoids hot surfaces, maintaining homogeneous heating conditions. The short residence times produced by pulsed CO_2 laser heating simplify product distributions, making them more tractable for detailed modeling.

LPHP combined with detailed kinetic modeling has been used to elucidate the kinetics of 1,3-butadiene (1,3-C_4H_6) pyrolysis over the temperature range of 800-1500K. Reaction temperatures are calculated from measured energy deposition into the sample (1,3-C_4H_6, SF_6 and He), the heat capacity of the mixture and calibrations using cyclobutanone as a chemical thermometer[2]. Residence times are estimated from the calculated temperature and known kinetics of cyclobutanone under these conditions[3]. The predominant reaction products are C_2H_4, C_2H_2 and C_4H_4 (vinyl acetylene), with significant quantities of C_6H_6. The basic mechanism used to understand 1,3-C_4H_6 pyrolysis is presented in Fig. 1.

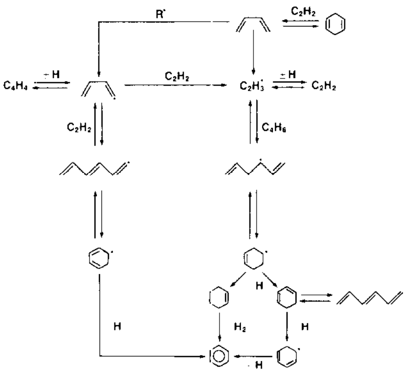

Fig. 1 Basic mechanism for 1,3-C_4H_6 pyrolysis. Initiation also occurs via 1,3-C_4H_6 → CH_3 +C_3H_3.

Initial unimolecular decomposition of 1,3-C_4H_6 produces C_2H_3, CH_3 and C_3H_3 radicals[4-6]. The ensuing important radical reactions in the LPHP experiment are either hydrogen abstraction to produce butadienyl radicals (C_4H_5) or C_2H_3 addition to 1,3-C_4H_6 to give cyclohexadiene and ultimately C_6H_6. Alternatively, subsequent reaction of C_4H_5 with C_2H_2 also gives C_6H_6 as the major product. In either route to C_6H_6 the chemical activation dynamics of high temperature exothermic reactions must be included to correctly account for C_6H_6 formation on the time scale of the experiment[7].

These competing reaction pathways are modeled, and found to be especially sensitive to the heats of formation of the vinylic radicals.

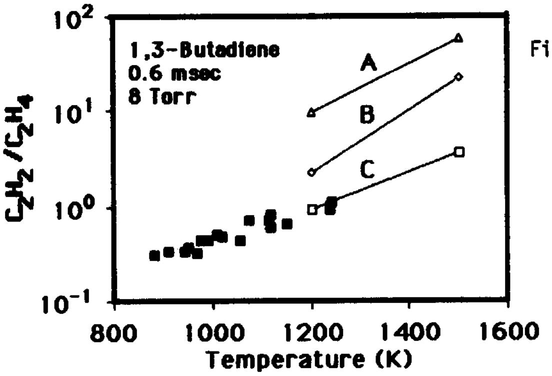

Fig. 2 Measured product ratio of C_2H_2/C_2H_4 from laser powered homogeneous pyrolysis of butadiene (solid squares). Shown for comparison are model calculations for butadiene pyrolysis which are seen to depend critically on the thermodynamic and kinetic parameters of vinylic species (See text).

Fig. 2 shows the product ratio C_2H_2/C_2H_4 determined experimentally and compares these measurements to model calculations varying the C_2H_3 stability.

When the usually accepted value of the heat of formation for vinyl radical is used (70 kcal/mole, curve A)[8], a very poor fit to the data is obtained. Reducing the heat of formation as suggested by recent shock tube data to 63 kcal/mole[4] (curve B) leads to a better fit, and the best fit is obtained with both a lower heat of formation and a reduced pre-exponential factor for vinyl radical dissociation[8]. The optimum pre-exponential factor determined in this work is in the range 0.3 - 3 x 10^8 sec^{-1}. This is substantially lower than the value 3 x 10^9 sec^{-1} estimated from a fall-off calculation[9] assuming a high pressure value of 1.2 x 10^{13} sec^{-1}. (curve C).

References

1. D. F. McMillen, K. E. Lewis, G. P. Smith and D. M. Golden, J. Phys. Chem., 86, 709 (1982); R.L. Woodin and K.A. Kajkowski, Proc. SPIE, 458, 28 (1984).
2. C. Steel, V. Starov, R.Leo, P. John and R.G. Harrison, Chem. Phys. Lett., 62, 121(1979).
3. A.T. Blades, Can. J. Chem., 47, 615(1969).
4. J.H. Kiefer, H.C. Wei, R.D. Kern and C.H. Wu, Int. J. Chem. Kinet., 17, 225 (985).
5. J. Collin and F.P. Lossing, Can. J. Chem., 35, 778(1957).
6. R.L. Woodin and C.F. Meyer, presented at the 190th National Meeting of the American Chemical Society, Chicag, IL, Sept. 8-13, 1985.
7. A.M. Dean, J. Phys. Chem., 89, 4600(1986).
8. D. F. McMillen and D.M. Golden, Ann. Rev. Phys. Chem., 33, 493 (1982).
9. A.M. Dean, unpublished results.