

ESR STUDY OF BIBENZYL DURING PYROLYSIS WITH AND WITHOUT HYDROGEN. Ralph Livingston and Henry Zeldes, Chemistry Division, Oak Ridge National Laboratory,\* Oak Ridge, Tennessee 37830 and Lonnie W. Vernon, Exxon Research and Engineering Company, P. O. Box 4255, Baytown, Texas 77520

Free radicals have been observed during pyrolysis of bibenzyl in solution and in an earlier report (R. Livingston, H. Zeldes, and M. S. Conradi, *J. Amer. Chem. Soc.* 101, 4312 (1979)) the equilibrium  $C_6H_5CH_2CH_2C_6H_5 + C_6H_5\dot{C}H_2 \rightleftharpoons C_6H_5\dot{C}HCH_2C_6H_5 + C_6H_5CH_3$  was described. The fluid sample at high pressure is circulated through a heated quartz capillary located in the ESR cavity where the contact time at pyrolytic temperature is approximately 0.5 sec. Dilute bibenzyl in toluene gives a spectrum of predominantly  $C_6H_5\dot{C}H_2$ , whereas in an inert solvent (benzene)  $C_6H_5\dot{C}HCH_2C_6H_5$  predominates. In the present study 0.1 to 1 M bibenzyl in toluene and in benzene have been studied from 507°C to 553°C at 1300 psi. The ESR spectra have been examined to verify radical content and samples have been collected after pyrolysis for GC. Where  $C_6H_5\dot{C}HCH_2C_6H_5$  predominates the usual distribution of products reported for bibenzyl (M. Poutsma, *Fuel*, 59, 335 (1980)) are seen with strong contributions from radical-radical coupling products. Where  $C_6H_5\dot{C}H_2$  predominates the product distribution alters greatly and the burnup of bibenzyl falls to 1/3 to 1/7 the value in benzene solution depending on concentration and temperature. High pressure hydrogen has been injected prior to pyrolysis and substantial increases in the yields of benzene and ethylbenzene have been observed. \*Research at this laboratory was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy, under Contract W-7405-eng-26 with Union Carbide Corporation.