

RELATIVE RATES FOR HYDROGEN DONATION TO BENZYL RADICAL

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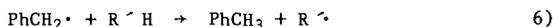
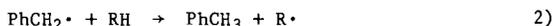
The hydrogen donating ability of coal liquefaction solvents is often cited as a prime factor affecting both liquefaction yields and product quality. A current discussion of liquefaction mechanisms has recently been published (1). The influence of hydrogen donors is generally interpreted according to the free radical mechanism of liquefaction first explicitly stated by Curran, Struck, and Gorin (2). According to this view, free radicals generated in coal by thermolytic reactions are quenched in greater or lesser amounts depending upon the availability of donable hydrogen. Previous work in this laboratory (3) has employed the benzyl radical as a model hydrogen acceptor with which to evaluate the relative ability of liquefaction solvents to donate hydrogen. Benzyl radicals were generated in the presence of donor solvent by the thermolysis of either dibenzylidiazene or dibenzylmercury at the relatively moderate temperature of 170°C. A portion of the benzyl radicals formed toluene by hydrogen abstraction from solvent; the amount of toluene reflected the relative donor strength of the solvent. In addition, sizeable portions of the benzyl radical dimerized, forming bibenzyl; and other portions added to or combined with the solvent. Preliminary evidence was found that the yields of toluene produced in different coal-derived solvents could be correlated with liquefaction yields obtained by standard microautoclave tests of coal liquefaction activity.

Detailed kinetic analysis of these experimental results was hampered by the side reactions of benzyl radical, in particular, dimerization and combination with solvent. The overall performance of a solvent is governed by a blend of many properties. To understand the influence of each property, it is necessary to isolate and separately evaluate the effect of different variables. Of primary interest is knowing the relative rate constants for hydrogen abstraction by benzyl radical from known or potential donor molecules. A method for obtaining such data is described here.

Relative rates of hydrogen abstraction have been measured by allowing donors to compete with a reference donor for benzyl radical. The method follows that used by Pryor et al. (4) for determining the reactivity patterns of the methyl radical with various hydrocarbons. The source of benzyl radical for the present experiments was dibenzylmercury. Rate constants for its thermal decomposition have been measured (5). Triphenylsilane deuterated at the silyl position was selected as the reference donor. This compound is a reactive donor and is readily prepared in the deuterated form by the reaction of triphenylsilylchloride with LiAlD₄.

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The competition experiment is summarized by the following set of equations:



RH represents the donor compound whose activity is to be measured. R' H represents all other sources of hydrogen in the system. Primarily, these are minor contributors, including solvent, reaction products, and impurities. Under pseudo-first order conditions for reaction with the reference donor and the donor compound in question (RH), the ratio of toluene to deuterio-toluene is given by the following:

$$\frac{[\text{PhCH}_3]}{[\text{PhCH}_2\text{D}]} = \frac{k_2 [\text{RH}]}{k_3 [\text{Ph}_3\text{SiD}]} + \frac{k_6 [\text{R}'\text{H}]}{k_3 [\text{Ph}_3\text{SiD}]}$$

The desired measure of relative reactivity, the ratio of rate constants k_2/k_3 , is taken as the slope of the plot of $[\text{PhCH}_3]/[\text{PhCH}_2\text{D}]$ versus $[\text{RH}]/[\text{Ph}_3\text{SiD}]$. The intercept is proportional to the concentration of hydrogen sources other than the donor compound.

The decompositions of dibenzylmercury were carried out in sealed stainless steel microreactors of about 2.5 mL capacity. The solvent was t-butylbenzene. This solvent was previously found to have negligible hydrogen donor capacity (3). Solutions were heated to 170°C for 18 hours, which assures complete extinction of dibenzylmercury based on calculations using published rate constants for dissociation (5). In a typical experiment, 0.1 mmol dibenzylmercury was decomposed in the presence of 1.0 mmol triphenylsilane-d and from 0.5 to 10 mmol of hydrogen donor compound.

After reaction was complete, the toluene produced was analyzed for deuterium content either by direct injection of the total product on GC/MS or by prior isolation of the toluene by GC, followed by analysis using high resolution mass spectrometry. Essentially identical results were obtained when the two methods were compared.

A plot of data for tetralin is shown in Figure 1. As may be seen, the expected linear relationship is found. The correlation coefficient for the straight line found by the least squares method is 0.997. From the slope of the line, the ratio of rate constants k_2/k_3 is determined to be 1.17 in the case of tetralin. Evaluation of relative rate constants for other donors is currently underway.

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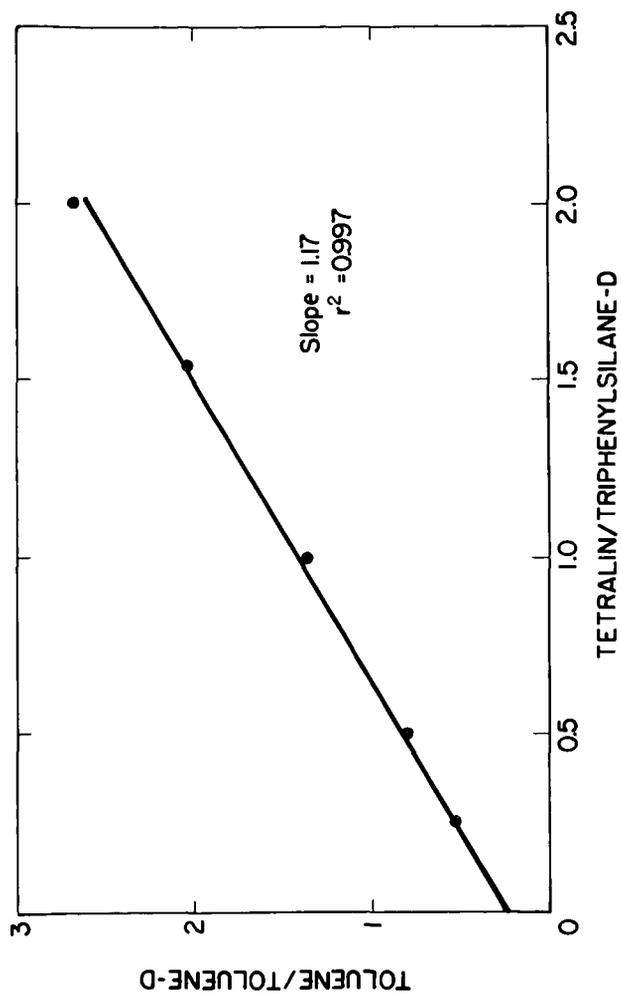


Figure 1. Determination of ratio of rate constants for abstraction of hydrogen from tetralin and deuterium from triphenylsilane.

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