

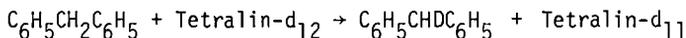
The Catalysis of the Exchange Reactions Between Tetralin- $d_{12}$  and Diphenylmethane by Inorganic Compounds

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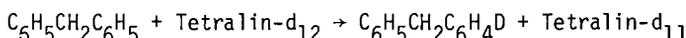
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Introduction

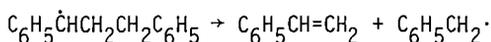
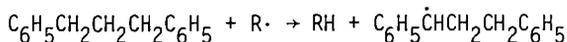
An array of inorganic compounds have been investigated as catalysts for coal gasification reactions (1,2). The pathways by which these compounds alter the rate and the product distributions in the gasification reaction have not been fully resolved. Whether the most effective catalysts promote the initiation reactions which occur at the threshold temperatures or the rapid gas forming reactions at the higher ultimate temperatures has not been established. We sought to resolve this point by an investigation of the influence of inorganic substances on the exchange reactions between the hydrogen atoms in the benzylic positions and the hydrogen atoms in the



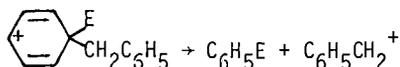
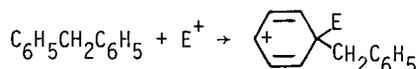
aromatic positions. These exchange reactions proceed slowly at 400°C in the



absence of catalysts (3). Both of these reactions may contribute in an important way to the breakup of the coal structure during the gasification reactions shown for the radical initiated decomposition of a 1,3-diphenylpropane:



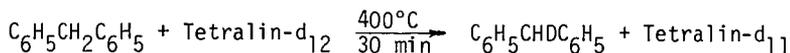
and the acid-catalyzed decomposition of a diphenylmethane with an electrophilic agent,  $E^+$



In the absence of a catalyst at 400°C, the free radical exchange reaction between the hydrogen atoms in the benzylic positions occurs much more readily than the exchange reactions of the hydrogen atoms bonded to the aromatic ring (3). Accordingly, we sought evidence for the acceleration of either process in the presence of inorganic compounds.

### Results and Discussion

In each experiment, diphenylmethane (0.377 mole) and tetralin-d<sub>12</sub> (0.377 mole) and a potential catalyst (0.045 mole) were sealed in a glass reactor at ambient temperature. The reactor was submerged in a fluid sand bath at 400°C for the desired reaction interval. After cooling, the organic contents of the reactor were separated from the inorganic reagents and analyzed by gas chromatography and nuclear magnetic resonance. The exchange reaction proceeds to give about 15% of the monodeuterio com-



15%

pound in 30 minutes in the absence of a catalyst. Lithium, sodium and potassium chloride are ineffectual as expected. Similarly, sodium fluoride, chloride, bromide and sulfate did not accelerate the exchange reactions. Sodium iodide enhanced the benzylic exchange reaction to a minor extent (22%). Iodine and hydrogen iodide accelerate the reaction to a much greater extent.

Lithium, sodium, and potassium carbonate and sodium and potassium bicarbonate do not enhance the exchange reactions. Thus, none of the alkali metal compounds exert any catalytic influence on this exchange reaction at the threshold temperature of 400°C.

Somewhat similar results were realized with the alkaline earth compounds. Neither calcium oxide or carbonate or barium carbonate or oxide enhance the exchange reaction. Calcium and magnesium chloride are also ineffectual catalysts for the exchange reaction after a 30 minute reaction. However, our preliminary results for reactions carried out for 120 minutes suggest that magnesium chloride enhances the rate of the exchange of the hydrogen atoms of the aromatic nucleus but not the benzylic exchange reaction.

Zinc halides also exert an accelerating influence on the rate of exchange of both the aliphatic and aromatic hydrogen atoms.

Compound	%D in Recovered Diphenylmethane		%D in Recovered Tetralin		
	Ar	$\alpha$	Ar	$\alpha$	$\beta$
ZnCl <sub>2</sub>	12	9	54	88	86
ZnI <sub>2</sub>	37	40	40	28	52

Whereas cadmium chloride is inactive, compounds such as stannous chloride and stannic chloride selectively enhance the rate of exchange of the aromatic hydrogen atoms of diphenylmethane and tetralin-d<sub>12</sub> at 400°C. Anhydrous vanadium trichloride and ferric chloride and hydrated chromous chloride and hydrated cupric chloride exert a similar effect on the reaction.

Compound	%D in Recovered Diphenylmethane		%D in Recovered Tetralin		
	Ar	$\alpha$	Ar	$\alpha$	$\beta$
SnCl <sub>2</sub>	19	0	28	91	91
CuCl <sub>2</sub> ·2H <sub>2</sub> O	24	5	44	92	92

Other highly reactive compounds such as aluminum chloride and molybdenum (V) chloride cause extensive reactions of the diphenylmethane and the tetralin. Moreover, oxidizing agents, for example, the oxides of lead and iron convert diphenylmethane to benzophenone.

The results obtained at the threshold temperature of 400°C strongly suggest that catalysts can selectively initiate free radical or electrophilic decomposition reactions of many coal molecules. The diverse character of the results will be emphasized in the presentation.

#### References

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