

THE INFLUENCES OF MACERALS ON THE HYDROGEN-DEUTERIUM
EXCHANGE REACTION BETWEEN TETRALIN AND DIPHENYLMETHANE

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INTRODUCTION

The concept that free radical reactions predominate during coal dissolution reactions is quite widely accepted (1). Recent findings concerning the selective and reversible abstraction reactions of hydrogen atoms from tetralin by radicals formed during the thermal decomposition of Illinois No. 6 coal at 400°C support this interpretation (2). The fact that weak organic acids and bases have only a modest influence on the rates of the exchange reactions of aromatic, aliphatic, and benzylic hydrogen atoms under these conditions whereas compounds such as benzyl phenyl ether, benzyl phenyl sulfide, thiophenol, the BDPA radical, anthraquinone, anthrone, tetra-cene, and acridine actively promote the benzylic exchange reactions are also in accord with the view that radical processes dictate the outcome of coal dissolution (2). Indeed, benzyl phenyl sulfide and thiophenol significantly enhance the rate of dissolution of Illinois No. 6 coal (3). The interactions between coals and donor molecules such as tetralin have been examined in several laboratories to improve the understanding of these reactions (2,4-6). However, no information concerning the re-activity of coal macerals in such situations has been available. Accordingly, we have compared the influences of maceral concentrates of some selected coals on the exchange reactions between tetralin-d₁₂ and diphenylmethane.

EXPERIMENTAL PART

The macerals used in this study were obtained from G. R. Dyrkacz and R. E. Winans of the Argonne National Laboratory. Some of the samples were prepared by density gradient centrifugation and others were prepared by float-sink techniques. The coal particles in all these samples were milled to three micron diameter and the separations were conducted in the presence of a surface active agent, polyoxyethylene (23) lauryl ether, in cesium chloride solutions (7).

The exchange reactions were conducted using a degassed solution of diphenyl-methane (0.376 mmole) and tetralin-d₁₂ (0.376 mmole) and the maceral material (25 mg) in a sealed glass vessel under an argon atmosphere at 400°C. The reactions were carried out for different times depending upon the reactivity of the maceral.

The products were isolated and analyzed using high field nmr spectroscopy as previously described (2). However, the macerals incorporate deuterium during the reactions and the change in the deuterium content of tetralin-d₁₂ is emphasized in this report rather than the degree of incorporation of this isotope into diphenyl-methane. Control experiments indicated that neither polyoxyethylene (23) lauryl ether nor cesium chloride altered the rate of the exchange reactions between tetralin-d₁₂ and diphenylmethane.

The compositions of the macerals were determined by G. R. Dyrkacz. As already reported (7), the PSOC 106 maceral concentrates were greater than 90% pure. For PSOC-828, separation I, it was found that the exinite concentrate contained 91% exinite and 9% vitrinite; the vitrinite concentrate contained 4% exinite, 90% vitri-nite and 6% inertinite; the inertinite concentrate contained 62.5% vitrinite and 32.5% inertinite. For PSOC-1103, separation II, it was found that the exinite con-centrate contained 46% exinite, 50% vitrinite, and 5% inertinite; the vitrinite con-centrate contained 3% exinite, 93% vitrinite and 5% inertinite; the inertinite con-centrate contained 2% exinite, 16% vitrinite, 33% inertinite, and 50% other material--either semifusinite or pseudovitrinite. The data provided by the sample bank strongly suggest that this material is semifusinite.

RESULTS AND DISCUSSION

The exchange reactions of the macerals isolated from two hvB bituminous coals, PSOC-106 and PSOC-828, are presented in Tables 1 and 2, respectively.

Table 1. The influence of the macerals from PSOC-106 on the deuterium-hydrogen exchange reaction of tetralin-d₁₂ and diphenylmethane at 400°C^a

Maceral (mg)	Deuterium Content of Tetralin (%)		
	Aromatic Positions	Benzylic Positions	Aliphatic Positions
None	95.1	92.3	92.3
Exinite (25.3)	94.7	79.6	89.1
Exinite (24.9)	95.6	83.8	90.1
Vitrinite (25.6)	95.4	84.9	89.9
Vitrinite (25.4)	95.3	84.2	89.7
Inertinite (25.1)	95.1	86.7	89.3
Inertinite (25.2)	94.7	86.9	88.6

^aDiphenylmethane (0.376 mmole) and tetralin-d₁₂ (0.376 mmole) were reacted for 60 minutes in the presence of these macerals. The tetralin-d₁₂ used in these experiments contained 96.1, 96.8 and 93.7% deuterium at the aromatic, benzylic, and aliphatic positions.

Table 2. The influence of macerals from PSOC-828 on the deuterium-hydrogen exchange reaction of tetralin-d₁₂ and diphenylmethane at 400°C^a

Maceral (mg)	Deuterium Content of Tetralin (%)		
	Aromatic Positions	Benzylic Positions	Aliphatic Positions
Experimental Series A			
None	94.7	91.3	93.0
Demineralized coal (25.6)	94.1	82.5	90.8
Exinite (25.4)	94.3	75.9	90.6
Vitrinite (25.4)	94.1	80.0	90.9
Inertinite (25.8)	94.7	82.4	90.3
Experimental Series B			
None	95.7	92.2	92.7
Raw whole coal	95.0	75.8	89.2
Demineralized coal	95.0	80.2	89.6
Exinite	94.9	80.0	89.1
Vitrinite	95.5	81.1	88.8
Inertinite	94.9	81.5	87.5

^aDiphenylmethane (0.376 mmole) and tetralin-d₁₂ (0.376 mmole) were reacted for 60 minutes in the presence of these macerals. The tetralin-d₁₂ used in these experiments contained 96.1, 96.8 and 93.7% deuterium at the aromatic, benzylic, and aliphatic positions.

The exchange reactions of the macerals isolated from different coals are presented in Table 3.

Table 3. The influences of macerals isolated from different coals on the deuterium-hydrogen exchange reaction of tetralin-d₁₂ and diphenylmethane at 400°C ^a

Source of Maceral (mg)	Deuterium Content of Tetralin (%)		
	Aromatic Positions	Benzylic Positions	Aliphatic Positions
Experimental Series C, Vitrinites			
None	94.7	91.7	92.4
PSOC-828, separation I, (25.3)	94.3	81.5	89.1
PSOC-828, separation II (25.3)	93.9	76.3	87.8
PSOC-1103, separation I (25.1)	93.9	79.2	87.4
PSOC-1103, separation II (25.4)	93.5	77.9	88.1
Illinois No. 2, undemineralized (25.2)	94.1	78.7	90.2
Illinois No. 2, demineralized (25.2)	94.0	78.0	89.5
Experimental Series D, Exinites			
PSOC-828, separation I (25.1)	94.7	78.0	89.2
PSOC-828, separation II (25.1)	93.9	78.4	88.6
PSOC-1103, separation II (25.0)	94.1	77.9	87.4
Experimental Series E, Inertinites			
PSOC-828, separation I (25.4)	94.9	81.7	89.7
PSOC-828, separation II (25.4)	94.5	80.8	88.9
PSOC-1103, separation II (25.2)	94.3	76.5	89.4

^aDiphenylmethane (0.376 mmole) and tetralin-d₁₂ (0.376 mmole) were reacted for 60 minutes in the presence of these macerals. The tetralin-d₁₂ used in these experiments contained 96.1, 96.8 and 93.7% deuterium at the aromatic, benzylic, and aliphatic positions.

Collins and his coworkers reported that Illinois No. 6 coal reduced benzophenone to diphenylmethane (8,9). We have used this reaction to assay the reactivities of the macerals. The results are summarized in Table 4.

Table 4. The effectiveness of macerals isolated from different coals for the reduction of benzophenone at 400°C for 60 minutes ^a

Reducing Agent (mg)	Reduction (%)
Experimental Series F, PSOC-828, Separation I	
Tetralin (51)	1.0
Demineralized whole coal (5.2)	2.0
Exinite (5.2)	3.6
Vitrinite (5.1)	2.1
Inertinite (5.1)	1.9
Experimental Series G, PSOC-1103, Separation II	
Tetralin (51)	1.2
Demineralized whole coal (5.8)	3.9
Exinite (5.7)	3.5
Vitrinite (5.6)	3.2
Inertinite (5.8)	1.5

^aThe reaction solutions in glass vessels were degassed prior to the introduction of argon and sealing.

The highly purified macerals obtained from PSOC-106 selectively enhance the rate of the exchange reaction at the benzylic position of tetralin-d₁₂. The order of reactivity, exinites > vitrinites > inertinites, is clearly established for the macerals of this coal. The macerals also enhance the exchange reactions at the aliphatic positions of tetralin, but to a lesser degree. No significant exchange occurs at the aromatic positions of tetralin or diphenylmethane under the conditions of these experiments. It is notable that the ratio of benzylic to aliphatic exchange decreases as the degree of benzylic exchange decreases. The finding is compatible with the view that the radicals produced from the macerals of lesser reactivity, the inertinites in this instance, are less selective.

The observations for the exchange reactions of the somewhat less pure macerals obtained from PSOC-828 and PSOC-1103 have some features in common with the results for the pure macerals of PSOC-106. In all cases, the reaction occurs selectively at the benzylic positions. In addition, the same reactivity sequence, exinite > vitrinite > inertinite, is also observed for PSOC-828. However, the differences in reactivity are somewhat less sharply defined, possibly because the inertinite concentrate contains a large amount of vitrinite. In contrast, the inertinite fraction obtained from PSOC-1103 exerts a greater accelerating influence on the exchange reaction than does the vitrinite obtained from the same coal. Analytical data indicate that this inertinite fraction is especially rich in sulfur. Consequently, the high reactivity is not unexpected (3).

The results obtained in the reduction of benzophenone, although not without anomalies, are more regular than the results obtained in the exchange reactions. The reactivity sequence, exinite > vitrinite > inertinite, is observed for both PSOC-828 and PSOC-1103. Moreover, the inertinite concentrates from these coals are both moderately more reactive than tetralin.

This preliminary series of observations reveal that there are differences in the hydrogen donor capacity of the different macerals obtained from three different coals, however, the differences in reactivity in the test reactions used in our study are not highly pronounced.

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