NOTE

Hydrodehydroxylation and Hydrodehalogenation of Substituted Polycyclic Aromatics Using Carbon Catalysts

There is a renewed interest in carbon materials as potentially inexpensive and environmentally safe catalysts. While carbon materials have been known as catalysts with modest activity for many years (1, 2), more recent advances in material science have made possible the synthesis of very high surface area carbon materials. Some of these materials are highly active and selective catalysts for oxidation reactions (3–6), dehydrochlorination of alkyl chlorides (7) and selective cleavage of C–C bonds (8–10).

Our work in the area of coal liquefaction modeling has shown the ability of carbon black and other carbon materials to cleave C–C bonds in model compounds with chemical structure relevant to coal and petroleum resids. A very high selectivity (over 90%) was observed for the cleavage of the bond between a condensed polycyclic aromatic ring and the adjacent aliphatic carbon (8–10). This activity has been correlated to the positive surface charge on the carbon catalyst at the reaction temperature. A cation–radical mechanism has been proposed for the reaction (9, 10), with electron transfer from the polycyclic aromatic ring to the carbon surface as the initial step of the catalysis. The ability of a carbon black to transfer an electron from an adsorbed iodine anion to an Fe^{3+} cation has been demonstrated by Spiro (11).

This report describes our studies of the catalytic activity of carbon black in selective dehydroxylation and dehalogenation reactions under reductive conditions in the presence of a hydrogen donor. Porous carbons are active catalysts for the oxidative decomposition of halogenated hydrocarbons (7) to CO_2 and HCl. Our method, using a reductive medium, would allow for recovery of the carbon and hydrogen part of the molecules, a feature relevant to the effort to recycle waste into useful materials.

The reactants studied in this work are identified in Table 1. Compounds II and VII were obtained from TCI America. All other phenols, halogenated reactants, and solvents were from Aldrich Chemical Co. The catalyst was carbon black BP2000 from Cabot (8). The reactions were performed in sealed glass reaction tubes, follow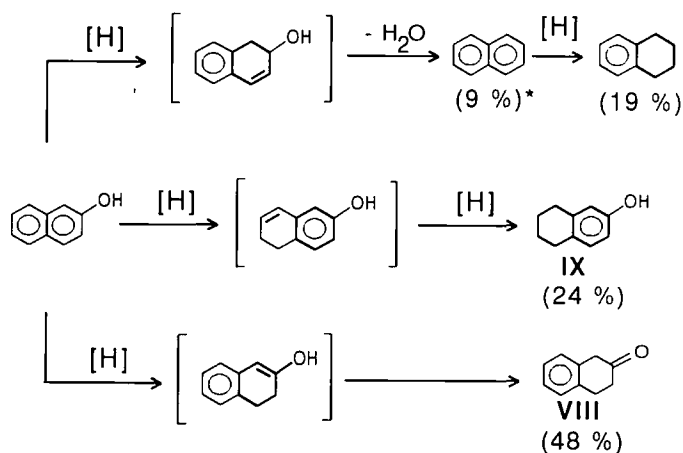ing the previously described procedure (9). Ratios of substituted aromatic to solvent to catalyst were 1 : 4 : 0.1. The H-donor solvent was 9,10-dihydrophenanthrene (9,10-DHP) in all cases except for I and II, where tetralin was used. The products were identified by GC–MS and quantified by GC, using a procedure described elsewhere (9). In selected cases (for III and IV) m-xylene was added as an integration standard to check the material balances, which were at least 95% in all cases.

A comparison of all the reactants studied is presented in Table 1 for reactions at 410°C. Reactivity and selectivity at various temperatures for the thermal and carbon-black-catalyzed reactions in the presence of 9,10-DHP are presented in Table 2 for compounds III and IV. Figure 1 shows the variation of conversion and yield of dehalogenation reaction products with time for the reaction of III at 400°C.

No chemical reaction is observed in the absence of an H-donor when III or V are heated at 410°C for 1 h, with or without carbon black. This is in contrast to the case of the C_{ar}–C_{aliph} selective bond cleavage in condensed polycyclic hydrocarbons (9, 10) where the cleavage was not affected by the presence or absence of an H-donor and where the C–C cleavage preceded any hydrogen transfer. The hydrogen transfer in that case was the subsequent step necessary for stabilization of the fragmentation moieties. In the case of dehalogenation and dehydroxylation reactions, the mechanism of the carbon-black-catalyzed reactions seems to require hydrogen transfer as the first step. A proposed mechanism for reaction of V is given in Scheme 1.

The selectivity of various products specified in Scheme 1 are from a reaction at 410°C, 1 h, and a 4 : 1 : 0.1 wt ratio of 9,10-DHP : V : BP2000. Under the same reaction conditions, the products obtained from III were naphthalene (50%), tetralin (23%), and chlorotetralin (27%).

The formation of tetralone (VIII) from 2-hydroxy-naphthalene (V) is a strong indication of the validity of the above reaction scheme. The product arises most likely from the tautomerization of 3,4-dihydro-2-naphthol, a vinylic alcohol formed when the first bond hydrogenated is C_3–C_4. It can be assumed that the analogous partially

SCHEME 1

[H] → [structure with OH] - H₂O → (9 %)* [H] → (19 %)

[structure]OH [H] → [structure]OH [H] → [structure]OH
IX
(24 %)

[H] → [structure]OH → [structure]O
VIII
(48 %)

SCHEME 1

hydrogenated products are formed in the case of chloro- and bromonaphthalene but are less stable to either further hydrogenation to the substituted tetralin product or dehydrogenation back to the initial reactant. If the first hydrogenated bond is C_1–C_2, the resulting allylic alcohol, 1,2-dihydro-2-naphthol, is rapidly dehydrated to naphthalene. If the first hydrogenation occurs at the unsubstitued ring in V, the corresponding olefin further hydrogenates to form the observed hydroxytetralin (IX). Schlosberg and Kurs (12) found a similar mechanism for the thermal reaction of 1-hydroxytetralin at 450°C under high hydrogen pressure. Formation of chlorotetralin and bromotetralin in the reactions of halogenated naphthalenes is a strong indication of a similar mechanism occurring for the halogenated compounds.

Data in Tables 1 and 2 show that both the degree of dehalogenation and dehydroxylation in various substituted aromatic compounds is substantially increased with an increase in the size of the aromatic system and is very dependent on the nature of the substituent. For the same aromatic moiety, bromo-substituted aromatics are more reactive than the corresponding chloro derivatives.

The selectivity data presented in Table 2 demonstrate that the catalyst activity for the dehalogenation reaction (formation of naphthalene plus tetralin) relative to its activity for the formation of halogenated tetralin shows little dependence on temperature. In addition, the ratio (naphthalene + tetralin)/halogenated tetralin is similar for both the thermal and catalytic reactions. The sequence of the reactions appears the same in both the thermal and catalytic reactions; hydrogen transfer from the H-donor solvent to the halogenated naphthalene, followed by elimination of HX if hydrogenation occurs at the substituted aromatic carbon (see also Scheme 1). This is in marked contrast with the results obtained in the cracking of aromatic hydrocarbons studied previously (9, 10), where a substantial difference was found between the selectivity of the thermal and the carbon-black-catalyzed reaction. For example, in the case of the cracking of 9-n-hexylphenanthrene, the selectivity at 410°C for the cleavage of the alpha bond is 22% for the thermal reaction and over 95% for the carbon-black-catalyzed reaction. In the case of hydrocarbons the selectivity is the same for cracking in the presence or absence of an added hydrogen donor. These differences in selectivity and hydrogen donor requirements between cracking and dehydroxylation or dehalogenation reactions clearly show that the carbon catalyst operates through different mechanisms in the two

TABLE 1

Hydrodehydroxylation and Hydrodehalogenation of Ar–X

Aromatic	X	Compound (No.)	Conversion (%)[a]	
			Thermal	BP2000
[structure]	OH	9-Hydroxyphenanthrene (I)	20	46
	Br	9-Bromophenanthrene (II)	20	95
[structure]	Cl	1-Chloronaphthalene (III)	13	50
	Br	1-Bromonaphthalene (IV)	17	64
[structure]	OH	2-Hydroxynaphthalene (IV)	12	50
[structure]	OH	4-Hydroxybiphenyl (VI)	4	4
	Cl	4-Chlorobiphenyl (VII)	2	5

[a] All Reactions at 410°C, 4 : 1 : 0.1 weight ratio solvent to Ar–X to catalyst.

TABLE 2

Halogenated Naphthalene Reactivity at Various Temperatures

Temperature (°C)	Conversion (%)		Selectivity (%)					
			Tetralin		Naphthalene		Halo-tetralin	
	Therm.	Catal.	Thermal	Catalytic	Thermal	Catalytic	Thermal	Catalytic
			1-Chloronaphthalene					
380	2	23	0	20	65	51	35	29
400	6	36	9	20	71	51	20	29
410	13	50	12	23	65	50	23	27
			1-Bromonaphthalene					
330	0	12	0	13	0	64	0	23
350	0	29	0	18	0	52	0	24
380	6	55	5	30	63	46	33	25
400	8	68	0	33	63	44	37	24
410	17	64	6	33	62	40	33	27

cases. Further studies are needed to establish the nature of the catalytically active sites on carbon black responsible for these substantially different results.

A mechanism involving halogen transfer from the haloarene to the carbon black appears unlikely under our reaction conditions (temperatures above 300°C and excess H-donor). It was shown (13) that chlorinated carbon materials actually lose chlorine upon heating under hydrogen at temperatures of 100–400°C. Moreover, hydrogen chloride was detected as a product in our reactions. The reuse of the same carbon black in four successive reactions of III in the presence of 9,10-DHP (1 h, 410°C) gave conversions of 51.2, 46.9, 43.9, and 41.1%, respectively, which demonstrates that carbon black is acting catalytically.

This work has shown that carbon black can catalyze dehydroxylation and dehalogenation reactions of aromatic compounds only in the presence of a hydrogen donor. The reactions are multistep processes that begin with hydrogenation through hydrogen transfer from a donor solvent. From the limited series of halogen derivatives investigated, it appears that the reaction rates increase with the size of the aromatic ring (cf. II and IV) and that bromo derivatives are more reactive that chloro derivatives (cf. III and IV). Chloronaphthalene and bromonaphthalene exhibit similar selectivities for thermal and catalytic reactions, in marked contrast with the very different selectivities of thermal and carbon-black-catalyzed C–C cleavage reactions reported previously.
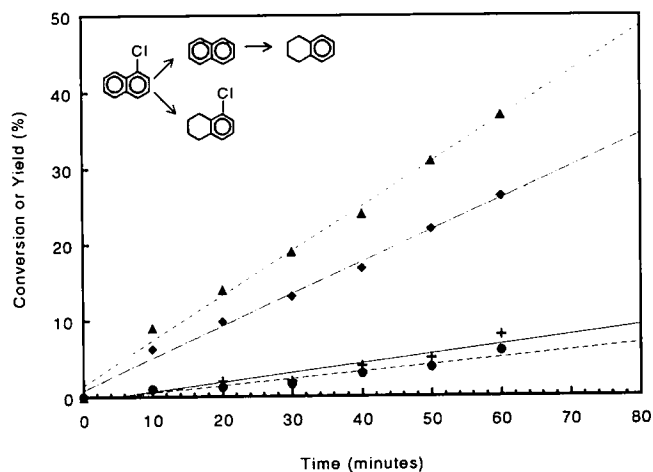
FIG. 1. Reaction of III as a function of time. Conditions: 400°C, sealed tube. Conversion: catalytic (▲); thermal (+). Dehalogenation yield: catalytic (◆); thermal (●).

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