THE USE OF o-TERPHENYL AND DIBENZO(c,g)PHENANTHRENE TO STUDY H-DONOR SOLVENTS

By

Eugene A. Kline
Tennessee Technological University
Cookeville, TN 38505

and

Bruce W. Farnum
Grand Forks Energy Technology Center
Box 8213, University Station
Grand Forks, ND 58202

The use of H-donors to increase yields of distillable liquids in direct coal liquefaction is well-documented (1,2,3). Several mechanisms have been proposed including the radical-trapping of hydrogen from the H-donors (4,5). Another mechanism suggested on the basis of thermochemical data (6) is a transfer of a hydrogen atom (radical) to an aromatic compound. This transfer is energetically favorable when specific atoms in the aromatic molecule are attacked. Phenanthrene, for example, is stabilized by 38 kcal/mole when attacked by a hydrogen radical to form the 9-hydrophenanthryl radical. This addition of hydrogen has not been studied to any extent at either of the model compound level or the process level.

Another reaction which may resemble the radical addition reaction was observed when 1,1'-binaphthyl was heated with an H-donor to form the thermally stable perylene (PER) (7). An H-donor was essential for coupling and different H-donors produced perylene in different yields. This reaction was used to study the relative ability of an H-donor to transfer its hydrogens at the high temperatures and pressures used in liquefaction. The coupling reaction appeared to have potential as a system to study this variety of H-transfer which may have important implications in the direct coal liquefaction process.

Problems encountered in this method of evaluating H-donors included the low yields of perylene and the low solubility of perylene in many solvents. Molar ratios of perylene to starting materials ranged from 1×10^{-2} to 28×10^{-2} after 1 hour reaction at 470°C. It was thought that a higher conversion of substrate would improve the reliability of the analytical method and would allow for shorter reaction times. One solution to the problem connected with the coupling to form perylene would be to find another molecule which would react by a similar mechanism but would give higher yields of a thermally stable product under similar reaction conditions. Copeland, Dean, and McNiel (8) reported that o-terphenyl (OTP) gave higher (60 pct) yields of coupled product, triphenylene (TP), than binaphthyl (18.7 pct) gave perylene when reacted with decalin at 490°C with a catalyst and hydrogen for 3 hours. Triphenylene was very stable and this reaction appeared to be a good alternative candidate for evaluation of H-donor reactivities. Several reactions were carried out with the o-terphenyl (Wiley Organics) and various H-donors at 470°C for 1 hour without hydrogen gas in small microreaction vessels. The results of these reactions are summarized in Table I and are compared to previously obtained results with 1,1-binaphthyl (7).

TABLE I

MOLAR RATIOS OF PRODUCT OF REACTANT FOR REACTIONS OF o-TERPHENYL AND 1,1'-BINAPHTHYL WITH H-DONORS AT 470°C FOR 1 HOUR*

H-Donor	TP/OTP x 10^{-2}	PER/BN x 10^{-2}
9,10-dihydrophenanthrene	2.05	3.1
1,2-dihydronaphthalene	2.47	3.4
1,2,3,4-tetrahydronaphthalene	2.51	1.3
fluorene	5.91	2.0
4,5-dihydropyrene	1.65	14.1
1,2,3,6,7,8-hexhydropyrene	--	28.0
indane	0.42	1.27
1,2,3,4-tetrahydroquinoline	0.37	--
1,2,3,4-tetrahydroisoquinoline	0.40	1.38
2,3-cyclohexenepyridine	0.88	--
indoline	--	3.84
5-indanol	0.49	1.24
indene	1.92	3.19

*Obtained by (Mole % coupled product)/(Mole % starting OTP or BN + sum of mole % of by-products)

The ratios of coupled product to starting materials were less satisfactory than those of binaphthyl in predicting H-donor ability. Some H-donors which promoted higher yields of perylene from binaphthyl also produced higher yields of triphenylene from o-terphenyl. There were exceptions including fluorene, 4,5-dihydropyrene and 1,2,3,6,7,8-hexhydropyrene which gave differing amounts of coupled product and in some cases even gave opposing trends. It was found with both substrates that many H-donors known to be good donors at lower temperatures did not give significant amounts of coupling at the higher temperatures used. This was particularly true of the heteroaromatic compounds with hydrogen attached to the heteroatom such as with 1,2,3,4-tetrahydroquinoline.

The conversion of o-terphenyl to triphenylene was not as great as expected based upon the three-fold yield of triphenylene over perylene (Equation 1). Moreover, very close to the peak of triphenylene in the gas chromatogram (using 6' x 2 mm ID 3 pct Dexsil 300 on Supelcoport 100/120 with programmed temperature) were several peaks analyzed by GCMS to be quatraphenyls (MW 306). Large amounts of biphenyl from the cracking of the terphenyl also reduced the possible yield of triphenylene and this complicated the analysis and the possible implications of the reactions to liquefactions.

Kinetics of the conversion of o-terphenyl to triphenylene were studied and compared with previous results of conversion of 1,1'-binaphthyl to perylene under similar conditions. The results are summarized in Table II.

TABLE II

PSEUDO FIRST ORDER RATE CONSTANTS FROM THE CONVERSIONS OF o-TERPHENYL AND 1,1'-BINAPHTHYL TO TRIPHENYLENE AND PERYLENE RESPECTIVELY

H-Donor	o-Terphenyl (k, min^{-1})	1,1'-Binaphthyl (k, min^{-1})
9,10-dihydrophenanthrene	7.0×10^{-3}	1.2×10^{-2}
1,2,3,4-tetrahydronaphthalene	7.4×10^{-3}	1.9×10^{-2}
1,2-dihydronaphthalene	---	---

The similarity between the products and the similar rate constants for each H-donor implied that the same mechanism was involved. When modeled as a first order reaction (Table II), o-terphenyl conversion was slower than binaphthyl conversion. It was interesting that 1,2-dihydronaphthalene formed no more coupled product with either binaphthyl or o-terphenyl after 45 minutes substantiating a similarity in the mechanism. The lower rate constants and the extra side products formed with o-terphenyl led to the conclusion that this system was less advantageous binaphthyl than coupling in the study of H-donor solvents.

Dibenzo(c,g)phenanthrene (DBP) (Equation 1) was investigated as another substrate likely to be a substitute for o-terphenyl and binaphthyl. Its structure suggested the possibility of facile coupling which could lead to enhanced rates and greater yields of coupled products. Dibenzophenanthrene was synthesized by coupling 1-tetralone to bis-dialin (BD) which was then reacted with maleic anhydride (9,10). The adduct was then brominated, dehydrobrominated, decarboxylated, and finally dehydrogenated to the desired dibenzo(c,g)phenanthrene, (Equation 1).

The low yield (7.5% overall) of dibenzophenanthrene was quite poor compared to that in the synthesis of binaphthyl (60%) from the common intermediate, 1,1'-dialin. The final product separated on an alumina chromatographic column with petroleum ether was 89% (VPC) pure. A small amount of this compound was reacted with 9,10-dihydrophenanthrene in the microreactor under the usual conditions. The yield of 8% coupled benzo(1,12)perylene (BP) product was an order of magnitude larger than either triphenylene or perylene. The retention time of the coupled product, benzoperylene, of 20.5 minutes was significantly longer than the retention times of other peaks in this reaction or of any component found in hydrogenated anthracene oil used as an experimental H-donor. There appeared to be no side reactions except some transfer of hydrogen from H-donor to the dibenzophenanthrene. Thus preliminary results indicate dibenzophenathrene might have distinct advantages over binaphthyl or o-terphenyl and would provide a very promising system to apply to the study of H-transfer reactions.

ACKNOWLEDGEMENT

This work was supported bu US DOE Contract No. DE-AC18-80FC10205.

LITERATURE CITED

1. Warrack C. Willson, Curtis L. Knudson, Gene G. Baker, Tom C. Owens, and Donald E. Severson, Technology in the Use of Lignite, Tenth Biannual Lignite Symposium, Grand Forks, ND, May 30-31 (1979) p. 170.

2. A.M. Souby, T.M. Owens, and D.E. Severson, Am. Chem. Soc. Div. Fuel Preprints, 25 (1) 233 (1980).

3. D.D. Whitehurst, T.O. Mitchell, and M. Farcasiu, Coal Liquefaction, Academic Press, New York, NY, (1980) p. 205.

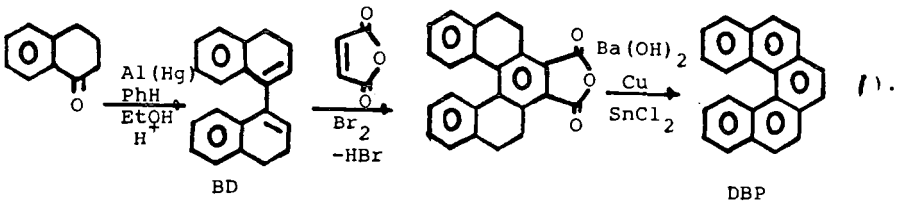
4. F.J. Derbyshire, P. Varghese, and D.D. Whitehurst, Am. Chem. Soc. Div. Fuel Preprints, 26 (1) 88 (1981).

5. Everett Gorin, Chemistry of Coal Utilization; Supplementary Vol 2, Martin A. Elliott, Ed., John Wiley and Sons, Ney York, NY (1981) p. 1882.

6. Stephen E. Stein, New Approaches to Coal Chemistry, B. Blaustein, B. Bockrath, and S. Friedman, Eds., ACS Ser. #169, Am. Chem. Soc., Washington, D.C. (1981) p. 113.

7. Eugene A. Kline, Mark E. Harrison, and Bruce W. Farnum, Am. Chem. Soc. Div. Fuel Preprints, 27 (3-4) 18 (1982).

8. P.G. Copeland, R.E. Dean, and D. McNiel, J. Chem. Soc., 1687 (1960).

9. F. Bergmann, E. Eschinazi, and M. Neeman, J. Am. Chem Soc., 65, 179 (1943).

10. H.A. Weislich, Ber., 71,1203 (1938).