

CLEAVAGE OF AROMATIC CARBON-CARBON BONDS

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Introduction

The search for a model substrate to use in evaluating relative reactivity of H-donors, under coal liquefaction conditions has led to this study of o-terphenyl.

The stability of biphenyl, terphenyls, quaterphenyls, and polyphenyls in the absence of H-donors has been demonstrated by their high bond dissociation energies between aromatic rings (1, 2). Therefore, they have practical application as coolant moderators in nuclear power plants (3). This stability is gained in part from the orbital overlap of the carbon atoms in the interannular C-C bond. The melting point of p-terphenyl is 208°C, and of hexiphenyl is 469°C. Their UV absorption at 278 and 318 nanometers, respectively, are indications of the increased stability as the number of benzene rings increases and resonance stabilization increases. The thermal temperature (defined as the temperature $\pm 10^\circ\text{C}$ at which decomposition rate is 1 mole % per hour) for m-terphenyl was 485°C and for the p-isomer was 478° (3). The same workers studying the problem of polymerization of polyphenyls and its control in nuclear power plants found one solution to the build up of the high molecular weight polymers. Reclamation by catalytic hydrocracking to reduce molecular weight in every case lowered the decomposition temperature to 320°-400°C due to formation of 20% methylated and ethylated products.

Reaction of polyphenyls under coal liquefaction conditions has been reported (4). The compound o-terphenyl (OTP) was found to couple irreversibly to form the very thermally stable triphenylene in the presence of an H-donor without a catalyst. Formation of different amounts of triphenylene with different H-donors suggested that o-terphenyl was a good candidate as a model substrate for study of the relative abilities of H-donors to react. Two other model substrates, 1,1'-binaphthyl (5) and dibenzo(c,g)phenanthrene (4), were also found to couple at different rates indicating they, too, would be possible substrates which could be used to differentiate the effectiveness of H-donors. Dibenzo(c,g)phenanthrene was difficult to prepare, and it coupled in the absence of H-donor and gave other hydrogenated isomers without coupling. o-Terphenyl formed extremely small amounts of coupled product compared to 1,1'-binaphthyl; consequently, the latter was judged to be the best model substrate of the three compounds to use in studying the effect of H-donors on the coupling reaction.

An unexpected result in the reaction of o-terphenyl and H-donors without catalyst was the large production of biphenyl. As much as 60%

cleavage reaction to yield biphenyl was observed while coupling reaction to yield triphenylene was always less than 5%. The rates of biphenyl formation varied with the particular H-donor used, suggesting that this cleavage reaction can be used to compare reactivity of H-donors at high temperatures. This paper discusses results of cleavage reaction studies with o-terphenyl.

Results and Discussion

All reactions were carried out in 1/2" Gyrolok, Parker, or Swagelok unions. Equimolar amounts of H-donor and o-terphenyl were added to the reaction vessel. It was filled with benzene solvent, and sealed without addition of a gas. The reactor was then placed in a fluidized sand bath controlled at $470 \pm 2^\circ\text{C}$. Analyses of the resulting product mixtures were carried out on a gas chromatograph programmed $75^\circ\text{--}300^\circ$ at $15^\circ/\text{min}$, 6' x 2 mm ID Dexsil 300 column.

The determination of kinetic rate constants provided some insight into the mechanism of the reaction. Reactions were run for 1, 2, 3, 4, and 5 hours with equimolar amounts of several model H-donors that were able to withstand the severe conditions. Mass balance was obtained in most cases accounting for both H-donor and o-terphenyl. The appearance of triphenylene and biphenyl were fitted to both first order and autocatalytic rate expressions. The best fit for the appearance of triphenylene was the autocatalytic rate expression; however, the first order expression correlated nearly as well. The formation of biphenyl appeared to fit the pseudo first order rate expression. The resulting yields and rate constants for the various H-donors with o-terphenyl to form triphenylene and biphenyl are shown in Table I.

The rate constants for the formation of triphenylene with different H-donors over five hours compared relatively well with the one-hour yield data. Hydrogenated heterocycles such as tetrahydroquinoline were too thermally-unstable to study under these conditions. The fact that triphenylene and biphenyl formation fit different rate expressions was significant. The autocatalytic formation of the coupled product (triphenylene from OTP) suggested that another species (perhaps the hydrogenated intermediate) was involved in the coupling. As this species was generated more coupling occurred.

A radical capping mechanism did not explain the kinetics data. Rather, coupling of the o-terphenyl by induction by a secondary H-donor seemed more justifiable. The 9,10-dihydrophenanthrene decomposed to a very small concentration within one hour (4), yet triphenylene continued to increase. Even in the case of tetralin which decomposed at a constant rate, there appeared to be autocatalytic formation of the coupled product.

Another way to investigate the mechanism was to study the differences and similarities of reactions of the isomeric terphenyls. Since cleavage was involved, the ortho-isomer had no predictable advantage as a model substrate. Two of the isomers, m-terphenyl and o-terphenyl were reacted with one H-donor, tetralin, for 1, 2, 3, 4, and 5 hours, and the products were analyzed by the usual method. p-Terphenyl was found to be quite insoluble in most solvents and reaction times of 1, 3, and 5 hours were selected. The results are summarized in Table II.

One deuterated H-donor 9,9,10,10-d₄-9,10-dihydrophenanthrene was reacted for three hours with o-terphenyl in benzene. The tendency toward random scrambling from the deuterated H-donor to the produced

biphenyl was studied by reacting the deuterated H-donor with biphenyl under the same conditions in a separate experiment. Due to excessive exchange, no clear cut mechanistic information was obtained.

The application of this reaction of o-terphenyl to determine relative reactivity of coal-derived liquids was studied by reacting equal weights of o-terphenyl and various start up and coal-derived recycle solvents produced in the UND Energy Research Center continuous process coal liquefaction pilot plant. The liquids used were from the ends of runs which had undergone several recycle passes in a reducing atmosphere, and which have been well characterized (6). The results of the reactions are summarized in Table III. The values of biphenyl produced were obtained by the difference of the biphenyl after reaction and the initial amount of biphenyl in the coal liquid.

The unique feature in the three hour o-terphenyl reactions was the formation of biphenyl in significant quantities in most cases and in differing amounts showing differences in the ability of the solvents to affect this cleavage. One thing noticeably different in running these reactions was the small amount of gas pressure in the reactor at the end of the reaction compared with the hydrogenated model H-donors.

In summary, o-terphenyl couples in the presence of model H-donors and many coal derived solvents to form triphenylene, and forms biphenyl by cleavage. The latter reaction is of more interest as the yields are substantial, and the yields have application to the study of properties of solvents. Attempts to elucidate the mechanism involved kinetic studies, and reaction with a deuterated H-donor. The best mechanism appears to be that in which the low steady-state concentration of reactive H-donor attacks either ipso position in o-terphenyl followed by cleavage (7). This mechanism is known to occur at high temperatures.

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Table I. Results of Reactions of H-Donors
and o-Terphenyl

| H-Donor | Triphenylene* | | Biphenyl** | |
|------------------------------------|---------------|-----------------------------------|------------|-----------------------------------|
| | Yield | k_3 (/sec) ($\times 10^3$) | Yield | k_3 (/sec) ($\times 10^3$) |
| Blank | 0.1 | -- | 3% | -- |
| 1,2,3,4-tetrahydro- naphthalene | 2.9% | 7.2 | 60 | 1.9 |
| 1,2-Dihydronaph- thalene | 2.7 | -- | 54 | 1.3 |
| 1,4-Dihydronaph- thalene | 2.5 | 6.4 | 4 | 1.3 |
| Fluorene | 2.9 | 1.6 | 60 | 1.4 |
| Indane | 7.1 | 9.8 | 30 | 2.5 |
| Indene | 3.7 | 8.5 | 46 | 1.8 |
| 9,10-Dihydrophen- anthrene | 3.2 | 7.0 | 34 | 2.6 |
| 9,10-Dihydroan- thracene | 1.0 | 3.3 | 47 | 1.6 |

*Triphenylene/initial OTP (one hour reaction)
(autocatalytic)

**Biphenyl/initial OTP (five hours reaction)
(Pseudo first order)

Table II. Results of Reactions of the Terphenyls with Tetralin at 470°C (rate constants - x 10³ min⁻¹)

| <u>o-Terphenyl</u> | <u>m-Terphenyl*</u> | <u>p-Terphenyl*</u> |
|--------------------|---------------------|---------------------|
| k=2.0 | k=2.4 | k=2.0 |

*Modelled pseudo-first order as best fit.

Table III. Results of Reactions of Coal Derived Liquids with o-Terphenyl at 470°C for 3 Hours

| <u>Coal Derived Solvent</u> | <u>Origin of Solvent</u> | <u>Biphenyl (RXN)- Biphenyl (INIT)</u> |
|---------------------------------|--|--|
| 101PB21 | Zap, ND lignite, pass 12 ^a | 68% |
| 101PB40 | Zap, ND lignite, pass 40 ^a | 37 |
| 67PB23 | Wyodak Subbituminous, pass 12 ^a | 5 |
| 64PB25 | Big Brown-Texas lignite, ^a pass 13 | 67 |
| 65PB23 | Beulah, ND lignite, 12 passes ^a | 67 |
| 53PB18 | Powhatan Bituminous, pass 18 ^a | 38 |
| Project Lignite Recycle Solvent | Zap, ND lignite, UND PDU | 28 |
| Crowley AO4 | Typical Anthracene Oil | 13 |
| SCR Mid. Dist. | Fort Lewis Pilot Plant (Powhatan coal) | 25 |

a) Recycle solvents from the University of North Dakota Energy Research Center continuous process unit.