If we refer to other recent studies of monodeuteriated six-membered rings, we must emphasize that the thermal variation of circular dichroism is weak with 3(*R*)-deuteriocyclohexanone,[26] more important for 5(*S*)-deuterio-2,2-dimethylcyclohexanone,[27] and very important for 3(*R*)-deuterio-2,2-dimethylcyclohexanone.[27] For these last two compounds, thermal variation analysis leads to $\Delta H^\circ = H^\circ_A - H^\circ_E < 0$, but we argue that the thermal variation may have been induced, in large part, by a vibronic effect like the one we have found in camphor.[2] Therefore, the difference between the cyclohexene and cyclohexanone results is not significant.

**Supplementary Material Available:** Tables S-II and S-III of rotativities of **5*S*** at −15 to 65 °C in *n*-heptane and *cis*-decalin and of **6*S*** at −15 to 65 °C in these solvents and in octane (2 pages). Ordering information is given on any current masthead page.

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[26] Sundararaman, P.; Djerassi, C. *Tetrahedron Lett.* **1978**, 2457.

[27] Lee, S. F.; Barth, G.; Kieslich, K.; Djerassi, C. *J. Am. Chem. Soc.* **1978**, *100*, 3965.

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# Pyrocondensation of Anthracene

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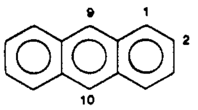
The predominant initial products in the thermal chemistry of anthracene are 2,9′-bianthracenyl and 9,10-dihydroanthracene. Over the range 350–500 °C, in the gas and liquid phase, this reaction follows second-order kinetics with $k/\text{M}^{-1}\ \text{s}^{-1} = 10^{7.37\pm0.27} \exp\{-22\,520\pm420/T\}$. The only other major product is 1,9′-bianthracenyl, which at low extents of reaction is formed at a rate one-seventh that of 2,9′-bianthracenyl. Anthracene selectively forms biaryls with the following compounds (relative rate constants for forming the major cross-biaryls are in parentheses): naphthalene (0.5), phenanthrene (0.2), biphenyl (0.2), diphenyl ether (0.2). A kinetic analysis of results leads us to propose that the initial step in these reactions is the reversible formation of a diradical via coupling of two ground-state molecules. This is followed by a rate-limiting, intramolecular H-transfer step resulting in a dihydrobiaryl molecule, which then rapidly loses two hydrogen atoms, probably by free radical reactions, to form the major biaryl products. Minor biaryl products are formed in a less selective manner in a reaction catalyzed by 9,10-dihydroanthracene. Aryl radicals are likely intermediates in these reactions.

## Introduction

Upon heating, hydrocarbons tend to decompose along two parallel pathways: one leads to small, thermally stable molecules, the other to a complex, intractable carbonaceous residue. Most studies of hydrocarbon pyrolysis have examined the former pathway. There now exists a large body of detailed kinetic data in this area as well as well-developed predictive ability. This advanced state is most evident in the case of paraffin pyrolysis, which, despite its considerable mechanistic complexity, is one of the best understood classes of reactions in chemical kinetics.[1]

On the other hand, relatively few chemical studies of reactions leading toward carbonization have been reported. Moreover, these studies have only rarely been done with the intention of deducing exact reaction mechanisms. As a result, while some general features of these reactions are known, mechanistic details, such as intermediates and rate-controlling steps, are largely unknown. We are now engaged in a program intended to clarify some of the basic features of these reactions. We report here studies of the "model compound" anthracene (An).

We chose to study anthracene pyrolysis for the following reasons. (1) A previous theoretical analysis suggested that "polymerization" might follow a straightforward free-radical pathway.[2] (2) Anthracene has only one highly reactive position, the meso (9 or 10) position, and therefore promised to react in a relatively simple manner. (3) Thermodynamic and kinetic properties of probable reaction intermediates were known or roughly estimable.[2,3] (4) Bianthracenyl isomers can be analyzed by gas chromatography.



Results of previous work on An pyrolysis are summarized below.

Several survey studies of a range of aromatic compounds[4,5] have concluded that as a neat liquid, An is a relatively reactive unsubstituted polyaromatic hydrocarbon which begins to decompose in the range 400–450 °C. It decomposed at least 100 times slower as a gas than as a liquid.[4]

In the early 1960s both Lang and Buffleb[6] and Badger et al.[7] examined An pyrolysis in gas-phase flow reactors with the aim of identifying products. Both groups reported 2,2′-bianthracenyl as a major reaction product near 700 °C and also reported products apparently formed by condensation of other bianthracenes. Reaction extents were rather high (>10% reported by Badger et al.), and unidentified tars were formed.

Walker and co-workers[8] used UV absorption to measure An disappearance rates at 490–509 °C over the applied pressure range 0.34–2.07 kbar. They found first-order kinetics from ~20% to >99% decomposition as well as a significant pressure dependence ($V = -17$ cm$^3$ mol$^{-1}$). Their reported Arrhenius expression was $10^{9.4}$ exp{−

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[1] See, for example: Albright, L. F.; Crynes, B. L.; Corcoran, W. H. *Pyrolysis: Theory and Industrial Practice*; Academic Press: New York, 1983. Allara, D. L.; Edelson, D. *Int. J. Chem. Kinet.* **1975**, *7*, 479.

[2] Stein, S. E. *Carbon* **1981**, *19*, 421.

[3] (a) Shaw, R.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1977**, *81*, 1716. (b) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

[4] Madison, J. J.; Roberts, R. M. *Ind. Eng. Chem.* **1958**, *50*, 237.

[5] Evans, S.; Marsh, H. *Carbon* **1971**, *9*, 733.

[6] Lang, K. F.; Buffleb, H. *Chem. Ber.* **1961**, *94*, 1075.

[7] Badger, G. M.; Donnelly, J. K.; Spotswood, T. M. *Aust. J. Chem.* **1964**, *17*, 1147.

[8] Whang, D. W.; Dachille, F.; Walker, P. L. *High Temp.-High Pressures* **1974**, *6*, 127.

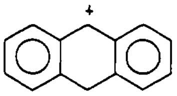
$23\,000/T\}\mathrm{s}^{-1}$ at 0.34 kbar, but Arrhenius parameters fell drastically with increasing pressure.

Lewis[9] has recently examined products of An pyrolysis under applied pressure at high extents of reaction with gel permeation chromatography and field-ionization mass spectroscopy. Dimeric, trimeric, and tetrameric anthracenes were found after pyrolysis at 440 °C for 4 h, indicating that the reaction proceeds through a normal, sequential polymerization mechanism.

With available pyrolysis data as a guide, one of us used thermochemical estimation methods to examine potential free-radical mechanisms in An pyrolysis.[2] Under most conditions in the liquid phase, the fastest path found involved addition of resonance-stabilized radicals to the 9-position of An, leading ultimately to 9,9′-bianthracenyl. In the gas phase, aryl radicals were predicted to be the most probable intermediates, resulting in more complex product distributions.

Carbonization of many polyaromatic substances can be catalyzed by halogen-containing additives. Morita et al.[10] reported that $CHCl_3$ and $CCl_4$ readily catalyze An carbonization at temperatures as low as 150 °C.

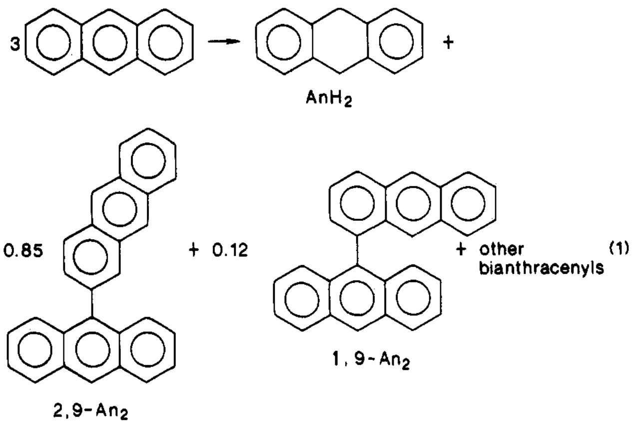
In a detailed study of catalyzed polyaromatic pyrolysis, Dworkin et al.[11,12] examined An decomposition in molten $SbCl_3$ at 150 °C. With liquid chromatography, NMR, and UV as analytical tools, 2,9′-bianthracenyl and 9,10-dihydroanthracene were identified as the major primary products. Two benzonaphthofluoranthenes, apparently resulting from condensation of 2,9′-bianthracenyl, were identified as major secondary reaction products. These workers directly observed the anthracenium cation by NMR.



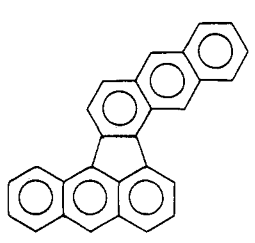
To establish the mechanism of An pyrolysis, we have examined this reaction over a wide range of conditions and in the presence of a variety of additives. Our major focus is on noncatalyzed reactions, although results of a limited number of catalyzed studies are also reported.

## Results

**A. Pure An Pyrolysis. Liquid.** The pyrolysis of liquid An was studied from 350 to 500 °C ($T_{\mathrm{critical}}$ ~610 °C[13]) and from extents of reaction from 0.02% to ~10%. Results are reported in Table I. At extents of reaction below ~2%, biaryl formation is described by reaction 1. The "other bianthracenyls" noted above are 1,2′-bianthracenyl (1,2-$An_2$), 1,1′-bianthracenyl (1,1-$An_2$), 9,9′-bianthracenyl (9,9-$An_2$), and 2,2′-bianthracenyl (2,2-$An_2$). Typically, only ~60% of detected $AnH_2$ could be attributed to hydrogen evolved during biaryl formation. This hydrogen imbalance is discussed later.



At higher extents of reaction, 2,9-$An_2$ decreased somewhat in relative concentration, although it remained the predominant biaryl product. A variety of partially hydrogenated species were observed above ~5% decomposition, including 1,2,3,4-tetrahydroanthracene and several di- and tetrahydrogenated biaryls, along with the two condensation products of 2,9-$An_2$ (benzonaphthofluoranthenes, $An_2H_{-2}$). One of the dihydrobiaryl peaks was not fully separated from 1,1-$An_2$. As a result 1,1-$An_2$ formation could not be reliably determined above ~1% reaction. Over the narrow range of conditions where it could be measured reliably, 1,1-$An_2$ was ~$^1/_5$ as large as 1,9-$An_2$.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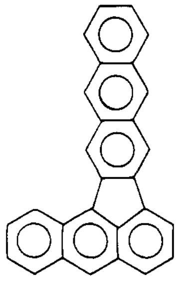
II

Several experiments determined noncondensible gas formation after pyrolysis for 1 h at 440 °C. They showed that on a molar basis, $H_2/AnH_2$ was at most 0.1.

Rates of 2,9-$An_2$ formation remained constant at a given temperature from the lowest extent of reaction measurable, ~0.02%, up to ~5% decomposition.

Biaryls were formed by nearly parallel processes at low extents of reaction, although most increased noticeably in concentration relative to 2,9-$An_2$ above ~1% decomposition. The only other primary product observed was an unidentified dihydrobianthracenyl species (denoted as $An_2H_2$). Apparent first-order rate constants for 2,9-$An_2$ formation, $k_{2,9}$(fo), obtained at low reaction extents are described by expression 2. This expression is based on data from Table I for decomposition <2%.

$$k_{2,9}(\mathrm{fo})/\mathrm{s}^{-1} = 10^{7.63\pm0.27}\exp\{21\,820 \pm 430/T\} \qquad (2)$$

**Gas.** Results of studies at 500 °C are given in Table II. Consistent with results of Madison and Roberts,[4] decomposition is much slower in the gas than in the liquid phase. While 2,9-$An_2$ is still the major product, it is not as predominant as in liquid-phase reactions. Concentrations of the minor biaryls relative to 2,9-$An_2$ were 2–10 times greater in the gas phase than in the liquid phase at comparable extents of reaction.

**B. An + Polyaromatic Compounds. Liquid.** A series of pyrolyses were done in which An was diluted with varying amounts of naphthalene and *p*-terphenyl to determine the reaction order for 2,9-$An_2$ formation. As shown in Figure 1, the formation rate of 2,9-$An_2$ is, within experimental scatter, second order in An. Therefore, 2,9-$An_2$ formation may be described by the following second-order rate constant

$$k_{2,9}/\mathrm{M}^{-1}\,\mathrm{s}^{-1} = 10^{7.37\pm0.27}\exp\{-22\,520\pm420/T\} \qquad (3)$$

This expression uses estimated temperature-dependent

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[12] Buchanan, A. C., III; Dworkin, A. S.; Smith, G. P. *J. Am. Chem. Soc.* **1980**, *102*, 5262.

[13] Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd, ed.; McGraw-Hill: New York, 1977.

**Table I. Liquid-Phase Anthracene Pyrolysis**[a]

| $T$, °C | time, min | runs[b] | $\frac{100[2,9\text{-An}_2]}{[\text{An}]}$ | $10^7 k_{2,9}^{\text{PFO}}$,[c] $s^{-1}$ | 100[product]/[2,9-$An_2$] | | | | | $\frac{[\Sigma \text{An}_2]}{[\text{AnH}_2]}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 9,9-$An_2$ | 1,9-$An_2$ | 1,2-$An_2$ | 2,2-$An_2$ | $An_2H_{-2}$[d] | |
| 350 | 580 | 2 | 0.10 | 0.29 | | 26 | 2 | | | 0.52 |
| 350 | 850 | 2 | 0.11 | 0.22 | 1.1 | 14 | 2 | | | 0.36 |
| 350 | 1095 | 2 | 0.13 | 0.20 | 0.8 | 12 | 1 | | | 0.34 |
| 350 | 1440 | 2 | 0.25 | 0.29 | | 21 | 2 | | | 0.60 |
| 380 | 10 | 1 | 0.0068 | 1.2 | | 15 | | | | 0.32 |
| 380 | 20 | 1 | 0.011 | 0.88 | | 14 | | | | 0.081 |
| 380 | 30 | 1 | 0.022 | 1.2 | | 13 | | | | 0.18 |
| 380 | 40 | 3 | 0.024 | 1.0 | | 14 | 2 | | | 0.39 |
| 380 | 50 | 2 | 0.027 | 0.90 | | 14 | | | | 0.52 |
| 380 | 60 | 1 | 0.037 | 1.0 | 0.6 | 15 | 1 | 2 | | 0.27 |
| 380 | 90 | 1 | 0.051 | 0.94 | 1.0 | 14 | 1 | 1 | | 0.42 |
| 380 | 100 | 2 | 0.054 | 0.91 | | 12 | | | | 0.36 |
| 380 | 120 | 1 | 0.071 | 0.98 | 0.9 | 14 | 1 | 2 | | 0.45 |
| 380 | 160 | 2 | 0.11 | 1.1 | | 13 | | | | 0.31 |
| 380 | 300 | 2 | 0.17 | 0.93 | 0.8 | 13 | 2 | | | 0.42 |
| 380 | 504 | 2 | 0.40 | 1.3 | 1.9 | 14 | 3 | 3 | | 0.47 |
| 410 | 5 | 2 | 0.014 | 4.9 | | 19 | | | | 0.44 |
| 410 | 10 | 2 | 0.027 | 4.6 | | 14 | | | | 0.38 |
| 410 | 20 | 2 | 0.063 | 5.3 | | 14 | | | | 0.55 |
| 410 | 40 | 2 | 0.15 | 6.2 | 0.6 | 14 | | | | 0.66 |
| 410 | 80 | 2 | 0.25 | 5.1 | 0.5 | 14 | 2 | | | 0.68 |
| 410 | 160 | 2 | 0.61 | 6.4 | 0.9 | 15 | 3 | | | 0.75 |
| 440 | 2 | 2 | 0.021 | 19.6 | | 20 | | | | 0.44 |
| 440 | 3 | 2 | 0.030 | 17.7 | | 15 | | | | 0.38 |
| 440 | 5 | 1 | 0.074 | 25.6 | 0.9 | 17 | 5 | | | 0.55 |
| 440 | 6 | 2 | 0.077 | 22.2 | | 15 | 2.4 | | | 0.55 |
| 440 | 8 | 2 | 0.091 | 19.5 | | 15 | 2.6 | | | 0.66 |
| 440 | 10 | 2 | 0.015 | 24.7 | 0.9 | 16 | 4.0 | | | 0.64 |
| 440 | 15 | 4 | 0.17 | 18.9 | 0.9 | 16 | 4.0 | | | 0.60 |
| 440 | 20 | 2 | 0.27 | 22.4 | 0.8 | 17 | 4.1 | | | 0.61 |
| 440 | 30 | 2 | 0.41 | 22.9 | 1.0 | 17 | 1.5 | | | 0.63 |
| 440 | 40 | 2 | 0.51 | 21.5 | 1.1 | 18 | 5.3 | 2 | | 0.67 |
| 440 | 60 | 8 | 0.89 | 24.8 | 1.7 | 22 | 6.0 | 3 | 1.0 | 0.92 |
| 440 | 80 | 2 | 1.2 | 24.3 | 1.6 | 20 | 7.2 | 5 | 0.58 | 0.76 |
| 440 | 90 | 1 | 1.3 | 24.9 | 1.9 | 22 | 8.2 | 4 | 2.8 | 0.65 |
| 440 | 120 | 1 | 1.7 | 24.3 | 2.3 | 23 | 7.3 | 7 | 3.7 | 0.73 |
| 440 | 140 | 1 | 2.5 | 30.2 | 2.6 | 24 | 9.7 | 9 | 4.9 | 0.95 |
| 440 | 160 | 2 | 2.6 | 24.4 | 2.7 | 26 | 10 | 3 | 12.4 | 1.15 |
| 440 | 180 | 1 | 2.2 | 23.5 | 2.5 | 25 | 9.1 | 1 | 3.3 | 0.66 |
| 470 | 2 | 2 | 0.073 | 67.3 | | 17 | 7.4 | | | 0.66 |
| 470 | 5 | 2 | 0.20 | 68.1 | 1.1 | 18 | 5.5 | 1 | | 0.71 |
| 470 | 10 | 2 | 0.39 | 67.1 | 1.1 | 19 | 4.9 | 3 | | 0.87 |
| 470 | 20 | 2 | 0.81 | 68.1 | 1.4 | 21 | 6.1 | 4 | | 0.84 |
| 500 | .5 | 1 | 0.038 | 211 | 2.6 | 17 | | | | 1.0 |
| 500 | 1 | 1 | 0.043 | 277 | 1.9 | 20 | 6.2 | | | 1.3 |
| 500 | 3 | 1 | 0.40 | 236 | 3.2 | 31 | 14 | 7 | 2.4 | 1.0 |
| 500 | 5 | 3 | 0.64 | 224 | 2.9 | 30 | 14 | 8 | 2.5 | 0.98 |
| 500 | 10 | 1 | 0.77 | 130 | 4.1 | 39 | 20 | 10 | 14 | 1.0 |
| 500 | 20 | 1 | 1.8 | 151 | 5.2 | 45 | 22 | 10 | 11 | 1.3 |

[a] Not given are 1,1-$An_2$ and an unidentified mass 356 peak (a dihydrobianthracenyl?) which were not fully resolved (see text). Above ~1% decomposition 1,1-$An_2$ was ~$^1/_5$ the size of 1,9-$An_2$. The dihydrobianthracenyl was comparable in size to 1,9-$An_2$ below ~0.1% reaction. [b] Number of different pyrolysis runs, data shown are averages. [c] Pseudo-first-order rate constant for 2,9-bianthracenyl formation; short-heating-time runs were corrected by 15 s for heat-up time. [d] Sum of two dibenzofluoranthene peaks (condensed 2,9-$An_2$). [e] Sum of all bianthracenyls.

**Table II. Gas-Phase Anthracene Pyrolysis (500 °C)**

| time, h | $10^2$[An], M | $\frac{100[2,9\text{-An}_2]}{[\text{An}]}$ | $10^6 k_{2,9}$, $M^{-1}$ $s^{-1}$ | 100[product]/[2,9-$An_2$] | | | | | $\frac{[\Sigma \text{An}_2]}{[\text{AnH}_2]}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 9,9 | 1,9 | 1,1 | 1,2 | 2,2 | |
| 2 | 2.1 | 0.075 | 5.0 | 3.1 | 43 | 11 | 26 | | 5.6 |
| 2 | 2.7 | 0.090 | 4.6 | 3.4 | 46 | 13 | 25 | | 3.5 |
| 2 | 3.2 | 0.11 | 4.8 | 2.6 | 37 | 10 | 27 | 3.3 | 2.7 |
| 2 | 3.7 | 0.079 | 3.0 | 1.6 | 32 | 7.5 | 24 | | 3.2 |
| 2 | 3.7 | 0.12 | 4.5 | 1.4 | 31 | 7.1 | 24 | 7.1 | 4.0 |
| 4 | 1.7 | 0.13 | 5.3 | 3.4 | 39 | 11 | 30 | 5.1 | 7.1 |
| 4 | 1.9 | 0.12 | 4.4 | 2.4 | 35 | 9.5 | 29 | 5.9 | 7.8 |
| 4 | 2.1 | 0.15 | 5.0 | 2.4 | 38 | 9.5 | 27 | 7.0 | 5.4 |
| 4 | 3.4 | 0.25 | 5.1 | 2.5 | 38 | 8.4 | 28 | 13 | 8.7 |
| 4 | 3.4 | 0.25 | 5.1 | 2.7 | 41 | 9.4 | 30 | 14 | 8.5 |

liquid densities.[13] Second-order kinetics is further supported by our observation that, within experimental error, at 500 °C $k_{2,9}$ is the same in the gas phase ($4.7 \times 10^{-6}$ $M^{-1}$ $s^{-1}$) as in the liquid phase ($5.0 \times 10^{-6}$ $M^{-1}$ $s^{-1}$). These measurements span a range of over 200 in An concentration.

When heated alone, both naphthalene and *p*-terphenyl were inert, but in the presence of An each became rather

Table III. Anthracene/Naphthalene Pyrolysis (440 °C for 1 h)

| [An], mol % | [Np], mol % | 100[2,9-An$_2$]/[An] | $10^7k_{2,9}$, M$^{-1}$ s$^{-1}$ | 100[An-Np$^a$]/[An] | $10^7k_{\text{cross}}$, M$^{-1}$ s$^{-1}$ | [1,9-An$_2$]/[2,9-An$_2$] | [An-Np$^1$]/[An-Np] | [An-Np$^{11}$]/[An-Np] | 100[ΣNp$_2$]$^b$/[Np] | 100[ΣAn$_2$]/[AnH$_2$] |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.89 | 99.1 | | | 0.16 | 0.72 | | 0.22 | 0.053 | 0.0077 | |
| 3.2 | 96.8 | 0.014 | 1.94 | 0.20 | 0.93 | 0.32 | 0.17 | 0.064 | 0.0083 | 0.032 |
| 8.3 | 91.7 | 0.082 | 4.47 | 0.28 | 1.39 | 0.25 | 0.21 | 0.057 | 0.021 | 0.14 |
| 13.3 | 86.7 | 0.12 | 4.23 | 0.32 | 1.71 | 0.21 | 0.24 | 0.087 | 0.031 | 0.12 |
| 23.7 | 76.3 | 0.24 | 4.91 | 0.33 | 2.10 | 0.18 | 0.25 | 0.10 | 0.039 | 0.24 |
| 31.1 | 68.9 | 0.31 | 5.30 | 0.29 | 2.11 | 0.18 | 0.25 | 0.12 | 0.040 | 0.31 |
| 45.9 | 54.1 | 0.37 | 4.23 | 0.25 | 2.42 | 0.17 | 0.21 | 0.11 | 0.024 | 0.58 |
| 59.2 | 40.8 | 0.54 | 4.01 | 0.18 | 2.38 | 0.21 | 0.24 | 0.11 | 0.026 | 0.49 |
| 84.1 | 15.9 | 0.70 | 4.95 | 0.072 | 2.69 | 0.21 | 0.23 | 0.13 | 0.018 | 0.61 |
| 100 | 0 | 0.98 | 6.11 | | | 0.20 | | | | 0.92 |

[a] An-Np denotes the major anthracene–naphthalene biaryl; An-Np$^1$ and An-Np$^{11}$ denote the second largest and third largest biaryl, respectively. [b] Sum of three isomeric binaphthalenyls.

Table IV. An/Aryl Studies, 440 °C

| Ar | $k_{\text{An-Ar}}/k_{2,9}$ | [An-Ar$^1$]$^a$/[An-Ar] | [other An-Ar$^b$]/[An-Ar] |
|---|---|---|---|
| biphenyl | 0.20 | 0.66 | <0.2 |
| diphenyl ether | 0.21 | 0.46 | <0.2 |
| phenanthrene | 0.23 | 0.75 | 1.5$^c$ |

[a] An-Ar$^1$ denotes the next largest diaryl. [b] Cross-biaryls other than An-Ar and An-Ar$^1$. [c] Eight other cross-products were also formed at a rate between 10% and 25% that of the major cross-biaryl (An-Ar).

reactive, forming biaryls with An (An-Ar) with a second-order rate constant one-fifth to one-half that of $k_{2,9}$.

The most thoroughly studied additive was naphthalene (Np). Two major cross-biaryls were formed; the one with the longer retention time, An-Np, was formed 4–5 times faster than the other, An-Np′. We have tentatively identified An-Np as 2-naphthyl-9-anthracene and An-Np′ as 1-naphthyl-9-anthracene (see Experimental Section for details). Table III shows that formation of these two biaryls is roughly first order in both An and Np down to ~25% Np and that the rate constant for forming An-Np is about one-half (0.47) of that for forming 2,9-An$_2$. Trace amounts of the three isomeric binaphthyls were also formed, but in a nearly statistical ratio (1,1′:1,2′:2,2′ = 0.7:2:1). An, in effect, catalyzed this reaction (no binaphthyls were observed in neat Np pyrolysis).

Reactions were also done in the presence of phenanthrene, biphenyl, and diphenyl ether. In each case, the major cross-biaryls were formed roughly half as fast as the major cross-biaryl in the An/Np reaction. Results are summarized in Table IV. In each case only two major biaryls were formed, although in the An/phenanthrene reaction a large number of minor biaryls were observed.

**Gas.** The product distribution resulting from the thermolysis of gas-phase An/Np mixtures was similar to condensed-phase results although relative concentrations of the major cross-biaryls were ~30% larger in the gas phase (Table V).

**C. Perdeuterated Anthracene (AnD) and Naphthalene (NdD) Studies.** A series of liquid-phase pyrolyses of neat An and An/Np (~50/50) mixtures were done at 440 °C for 30 min with both perdeuterated and protonated reactants. Relative rate constants for forming 2,9-An$_2$ and An-Np are given in Table VI. Mass spectral analysis indicated little (<5%) H/D scrambling.

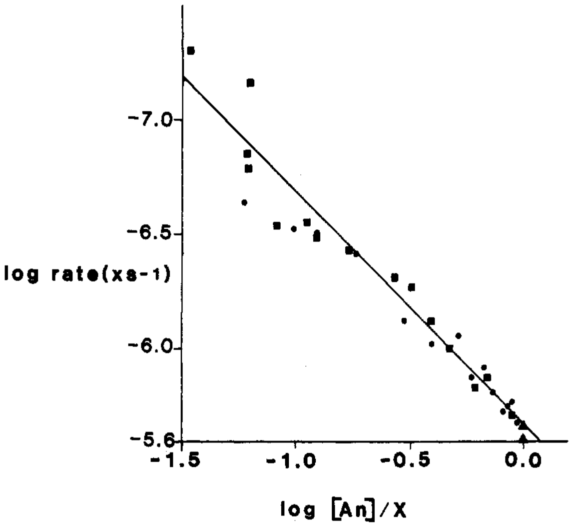


Figure 1. Pseudo-first-order rate constant for anthracene conversion to 2,9-bianthracenyl vs. the log of anthracene concentration (in mole fraction units) (440 °C, reaction times 15 min to 5 hours): ■, *p*-terphenyl; ●, naphthalene; ▲, neat. Line shows exact second-order kinetics.

Use of AnD in place of AnH (protonated) reduced $k_{2,9}$ by ~35% and with NpD in place of NpH reduced An-Np biaryl rate constants by nearly the same amount. With AnD in place of AnH had little effect on the rate of An-Np formation. These results suggest that the rate-limiting step in biaryl formation involves H-transfer. In the case of An-Np formation this step involves H-atom transfer from Np, not from An.

**D. Effects of Added AnH$_2$. Liquid.** A series of studies examined product distributions as a function of added AnH$_2$ in both An and An/Np reaction systems. Results are shown in Figures 2 and 3.

Table V. An/Np/AnH$_2$ Gas-Phase Studies, 500 °C

| time, h | $10^2$[An], M | $10^2$[Np], M | $10^2$[AnH$_2$], M | $k_{\text{An/Np}}/k_{2,9}$ | [product]/[2,9-An$_2$] 9,9 | 1,9 | 1,1 | 1,2 | 2,2 | [An-Np$^1$]/[An-Np] | [An-Np$^{11}$]/[An-Np] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2.5 | 0 | 0.9 | | 0.074 | 0.81 | 0.13 | 0.30 | 0.15 | | |
| 2 | 3.3 | 0 | 0.4 | | 0.059 | 0.68 | 0.20 | 0.20 | 0.069 | | |
| 2 | 2.7 | 0 | 0.9 | | 0.076 | 0.77 | 0.13 | 0.32 | 0.16 | | |
| 2 | 1.9 | 0 | 2.2 | | 0.081 | 0.81 | 0.10 | 0.36 | 0.097 | | |
| 2 | 2.0 | 2.3 | 0 | 0.53 | 0.028 | 0.60 | 0.13 | 0.25 | | | |
| 2 | 2.3 | 1.7 | 0.9 | 0.70 | 0.057 | 0.74 | 0.11 | 0.30 | | 0.37 | 0.06 |
| 4 | 2.7 | 0 | 1.1 | | 0.085 | 0.85 | 0.11 | 0.26 | 0.18 | | |
| 4 | 2.0 | 2.2 | 0 | 0.69 | 0.022 | 0.49 | 0.05 | 0.15 | | 0.40 | 0.34 |
| 4 | 1.9 | 2.0 | 1.0 | 0.56 | 0.036 | 0.68 | 0.10 | 0.20 | | 0.70 | 0.56 |

**Table VI. Kinetic Isotope Effects**[a]

| | $k^D/k^H$ | |
|---|---|---|
| | 2,9-$An_2$[b] | An-Np[c] |
| neat An | 0.63 | |
| $An^D/Np^H$ | 0.77 | 1.34 |
| $An^H/Np^D$ | 1.0 | 0.56 |
| $An^D/Np^D$ | 0.69 | 0.60 |

[a] H and D superscripts denote perdeuterated compounds. Each result is based on the average of two separate runs. The average deviation was ±12%. [b] This column contains $k_{2,9}{}^D/k_{2,9}{}^H$. [c] This column contains $k_{An\text{-}Np}{}^D/k_{An\text{-}Np}{}^H$.

Addition of $AnH_2$ had only a small effect on the formation of 2,9-$An_2$ and An-Np, a substantial effect on 1,9-An and An-Np′, and an even larger influence on the other biaryls. A comparison of Figure 2 with Table I indicates that changes in distributions of minor biaryls with increasing reaction extent in neat An pyrolysis were at least partly due to the buildup of $AnH_2$. The formation of binaphthyls in An/Np mixtures is particularly sensitive to the presence of $AnH_2$.

Studies of other additives (biphenyl, diphenyl ether, phenanthrene) also showed that formation rates of only the minor An-Ar adducts were strongly influenced by $AnH_2$.

**Gas.** In terms of product distributions, the addition of $AnH_2$ to gas-phase reactions had an effect similar to that for liquid-phase reactions, with the less significant cross-products increasing in relative concentrations (see Table V). However, since $AnH_2$ rapidly decomposed, presumably to An and $H_2$ (rather little $AnH_2$ was detected as a product), it appears that $H_2$ in the gas phase has an effect similar to $AnH_2$ in the liquid phase.

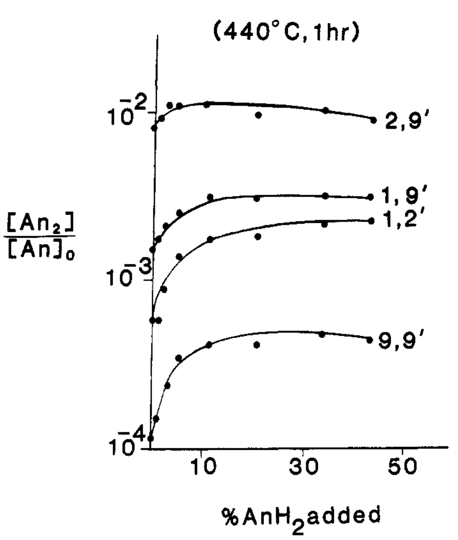


**Figure 2.** Bianthracenyl concentrations vs. initial amount of 9,10-dihydroanthracene (440 °C, 1 h).

**E. Halogen-Containing Additives.** Since halogen-containing compounds are known catalysts for aromatic carbonization, effects of a number of halogen-containing molecules on An pyrolysis were surveyed. Studies were done with molecular iodine as well as with a variety of halogenated polyaromatic molecules, all in the presence and absence of $AnH_2$. Several studies were also done in 50/50 An/Np mixtures. Illustrative results are given in Table VII.

Kinetics were complex and quantitative results were not highly reproducible. Some noteworthy aspects of these reactions are as follows. (1) Even trace amounts of halogen atoms significantly catalyze the reaction. (2) On a per-atom basis, all halogens have roughly the same degree of catalytic activity. (3) Pure 9-chloroanthracene and 9-bromoanthracene decompose readily on melting (~200 °C), yielding high concentrations of dimeric products. (4)

**Table VII. Halogen Additive Study**

| $T$, °C | time, min | wt % additive | $[AnH_2]_i/[An]$ | $100[2,9\text{-}An_2]/[An]$ | $[1,9\text{-}An_2]/[2,9\text{-}An_2]$ | $[9,9\text{-}An_2]/[2,9\text{-}An_2]$ | $[\text{biaryls}]/[AnH_2]$ |
|---|---|---|---|---|---|---|---|
| | | | | $I_2$ in MeOH $EtO_2$ | | | |
| 320 | 60 | 0.01 | | 0.40 | 0.25 | 0.20 | 0.86 |
| 350 | 60 | 0.01 | | 0.13 | 0.30 | 0.33 | 0.52 |
| 380 | 60 | 0.02 | | 1.2 | 0.38 | 0.86 | 0.33 |
| 380 | 10 | 0.005 | | 0.11 | 0.33 | 0.33 | 0.59 |
| 380 | 10 | 0.01 | | 0.46 | 0.30 | 0.30 | 0.74 |
| 380 | 60 | 0.10 | | 0.46 | 0.41 | 1.1 | 0.19 |
| 410 | 5 | 0.005 | | 0.25 | 0.30 | 0.30 | 0.76 |
| 410 | 15 | 0.005 | | 0.65 | 0.33 | 0.33 | 0.46 |
| | | | | $I_2$ in Toluene | | | |
| 410 | 5 | 0.1 | | 0.71 | 0.49 | 1.63 | 0.40 |
| | | | | 1-Iodonaphthalene in Toluene | | | |
| 410 | 5 | 0.1 | | 0.076 | 0.31 | 0.59 | 0.15 |
| | | | | $I_2$ in Toluene | | | |
| 410 | 5 | 0.1 | 5.0 | 0.82 | 0.45 | 1.21 | 0.29 |
| | | | | 1-Iodonaphthalene in Toluene | | | |
| 410 | 5 | 0.1 | 5.0 | 0.14 | 0.34 | 0.56 | 0.057 |
| | | | | 9-Chloroanthracene in Toluene | | | |
| 410 | 15 | 0.1 | | 0.60 | 0.28 | 0.16 | 0.32 |
| 410 | 15 | 0.5 | | 0.85 | 0.29 | 0.16 | 0.70 |
| 410 | 60 | 0.1 | | 0.25 | 0.22 | 0.08 | 0.43 |
| 410 | 15 | 0.1 | 5 | 0.33 | 0.32 | 0.15 | 0.14 |
| 410 | 60 | 0.1 | 5 | 1.85 | 0.26 | 0.09 | 0.39 |
| | | | | 9-Bromoanthracene in Toluene | | | |
| 410 | 15 | 0.02 | | 0.038 | 0.20 | 0.21 | 0.31 |
| 410 | 15 | 0.10 | | 2.77 | 0.19 | 0.08 | 0.42 |
| 410 | 60 | 0.02 | | 1.85 | 0.25 | 0.09 | 0.47 |
| 410 | 15 | 0.02 | 5 | 0.072 | 0.32 | 0.17 | 0.022 |
| 410 | 60 | 0.02 | 5 | 0.35 | 0.25 | 0.09 | 0.079 |

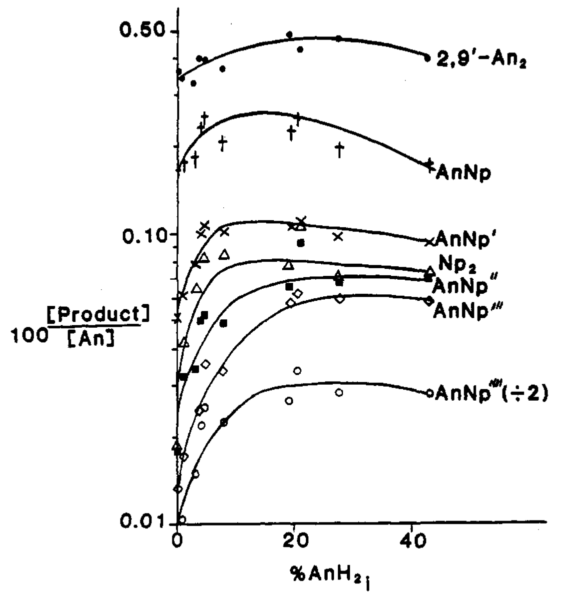


**Figure 3.** Biaryl concentrations vs. initial amount of 9,10-dihydroanthracene in 50:50 anthracene/naphthalene mixture (440 °C, 1 h). $Np_2$ represents total binaphthyl formation, An-Np( ) represents different naphthylanthracene isomers.

Distributions of bianthracenyls in catalyzed and noncatalyzed reactions were similar, with 2,9-$An_2$ as the predominant dimer in all cases. However, in the catalyzed reaction, 9,9-$An_2$ became a major dimer, in some cases comparable to 2,9-$An_2$. (5) The apparent hydrogen imbalance found in neat An pyrolysis was also observed in the catalyzed reactions.

**F. Impurities and Surface Effects.** Considerable effort was spent testing for the influence of impurities in An or of species evolved from Pyrex surfaces on the condensed-phase reaction. Most of these tests were done at 440 °C for 15 min and/or 30 min. Results were negative and are summarized below. (1) Extents of reaction and product distributions were identical in reaction tubes made of Pyrex, fused silica, gold, and stainless steel and in both small-scale (75 mg) and large-scale (3 g) pyrolyses. (2) Added Pyrex chips had no effect. (3) Results were the same with An directly from the original container, recrystallized (from methanol or tetrahydrofuran), or sublimed. Anthracene from three different manufacturers gave identical results. (4) Warming under evacuation prior to sealing had no effect nor did incomplete evacuation of the tube prior to sealing. (5) Addition of small amounts (~5%) of An oxidation products (9,10-anthraquinone and anthrone) did not have a significant effect. No effects were observed for a variety of organic additives including, tetracene, 9-cyanoanthracene, benzophenone, 1-naphthol, and 1,2-diphenylethane (a free radical initiator[15]).

**G. Mass Balance Studies. Carbon Balance.** Since the focus of the present work was on reaction at low extents of decomposition, neither internal nor external standards could be used to test for mass balance. This was done instead by weighing products of large-scale (3 g) pyrolyses. Two runs were done at 440 °C for 1 h and products were separated by sublimation, weighed, and then analyzed by gas chromatography (GC). Sublimation efficiently separated An and $AnH_2$ from less volatile products. These results indicate that our GC analysis accounted for >90% of high molecular weight products. The nonsublimed products were dissolved in tetrahydrofuran and analysis of this solution by normal and reversed-phase high performance liquid chromatography (HPLC) showed no unidentified peaks even after very long elution times. Gel permeation chromatography also showed no unexpected high molecular weight products. UV analysis of the dissolved product residue was just as expected on the basis of UV analysis of the individual peaks eluting from reversed-phase HPLC analysis.

**Hydrogen Balance.** As noted earlier, typically only ~60% of the evolved hydrogen (detected as $AnH_2$) could be attributed to the biaryl formation. This hydrogen imbalance was found in neat An pyrolysis, in all runs described in section F, as well as in both the halogen-catalyzed reactions and reactions involving diluents. It was most severe at the lowest extents of reaction.

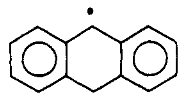
We could not find the origin of this problem. We suspect that the cause is either an undiagnosed problem in our analysis procedure or an undetected hydrogen-poor product being formed in parallel with aryl dimers. In any event, there is no evidence that this problem had any important bearing on the primary processes monitored in these experiments, namely, the formation of biaryls.

## Discussion

The simple, second-order kinetics observed for 2,9-$An_2$ formation over a wide range of conditions suggests the involvement of a simple, non-free-radical process. The weak rate dependence on radical concentration as well as the selectivity of biaryl formation also supports this view. However, complex chain reactions can also have integral reaction orders,[16] and hydrocarbon pyrolysis reactions most often involve free-radical reaction steps. Therefore, an analysis of potential free-radical mechanisms is given before considering less conventional pathways.

**A. Free-Radical Mechanisms.** In this section we show that neither the observed product distributions nor the reaction kinetics is consistent with a conventional free-radical mechanism. This analysis uses rate and thermodynamic data obtained or extrapolated from the literature as well as values estimated by available methods.[17-19] Two general pathways leading to biaryls will be considered. One path involves the addition of a resonance-stabilized radical to an aromatic molecule. In the other, the addition step involves an aryl radical.

**Addition of Stabilized Radicals.** In view of its considerable resonance stabilization energy,[17] the predominant free radical in An pyrolysis is expected to be the 9,10-dihydroanthracen-9-yl radical



AnH•

At 440 °C in neat An, the half-life of $AnH_2$ toward forming AnH· radicals in reaction 4, is ~5 s.[20] This re-

$$AnH_2 + An = 2AnH\cdot \qquad (4)$$

---

[14] Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply the material or equipment identified is necessarily the best available for the purpose.

[15] Stein, S. E.; Robaugh, D. A.; Alfieri, A. D.; Miller, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 6567.

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[17] McMillan, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

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[19] Stein, S. E. In *New Approaches in Coal Chemistry*; American Chemical Society: Washington, D.C., 1981; ACS Symp. Ser. No. 169, p 97.

action is therefore equilibrated in our experiments and serves as a steady source of free radicals.

Because of the stability of AnH·, its addition reactions will be highly reversible. On the basis of thermochemical kinetics calculations,[18,19] we estimate the net rate for irreversible addition to the 2-position in anthracene, leading to 2,9-$An_2$, to be a minimum of 100 times slower than the observed rate even under favorable conditions (high $An_2$ concentrations). Moreover, none of the mechanisms that we have been able to construct involving addition of resonance-stabilized radicals yield either the observed reaction order ($[AnH_2]^0[An]^2$) or product distribution.

**Addition of Aryl Radicals.** Because of their high reactivity[21] and probable involvement in gas-phase reactions of benzene,[22] aryl radicals are plausible intermediates in An pyrolysis. The following analysis, however, indicates that they are not involved in mechanisms leading to the major biaryl products. It does suggest, on the other hand, that they may be involved in the formation of minor biaryls.

Under the experimental conditions of this work, our rate estimates indicate that H-abstraction by AnH· (reaction 5) is the fastest generator of aryl radicals. This is a result

$$\mathrm{AnH\cdot} + \mathrm{An} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{AnH_2} + \mathrm{An\cdot} \qquad (5)$$

of its very low intrinsic activation energy (that is, the activation energy for its reverse reaction is small).

Our analysis indicates that the observed kinetics of forming the major diaryls is inconsistent with this aryl radical model, but forming minor diaryls by this means is feasible. All of the aryl radical mechanisms that we could devise had fractional order kinetics in both anthracene and $AnH_2$ under most conditions of the current experiments. At sufficiently low concentrations of $AnH_2$, all of these mechanisms predicted one-half order kinetics in $AnH_2$. Only the minor biaryls were formed with rates noticeably dependent on $AnH_2$ concentrations and with nonintegral reaction orders. For instance, in neat anthracene pyrolysis, after subtracting amounts formed in the limit $[AnH_2] = 0$, formation rates of the two major $AnH_2$-dependent bianthracenyls, 1,1-$An_2$ and 1,9-$An_2$, were both nearly one-half order with respect to $AnH_2$. Moreover, relative to 2,9-$An_2$, these products were more significant in the gas-phase reactions than in the liquid phase, suggesting a less than first-order dependence on An concentration. We therefore suspect that aryl radicals are involved in formation of the minor, $AnH_2$-dependent biaryls.

In addition to the above kinetic arguments, we find that regardless of the actual means of aryl radical formation, we cannot devise a reasonable aryl radical mechanism consistent with either the observed product distribution or its dependence on $AnH_2$ concentration. Aryl radicals are expected to add most readily to the 9-anthracene position. This was confirmed in our product identification studies (see Experimental Section). On this basis, to explain observations an aryl radical mechanism requires that the predominant aryl radical is 2-anthracenyl, with 1-anthracenyl one-seventh as significant and 9-anthracenyl one-hundredth as significant (this is based on the observation at low reaction extents that 2,9-$An_2$:1,9-$An_2$:9,9-$An_2$ = 1:1/7:1/100).

In summary, the above arguments indicate that conventional aryl radical mechanisms cannot account for the major products. For aryl radicals to be precursors of the major biaryls, they would have to be formed and react in a highly unusual manner and at a rate exactly second order in An. We cannot construct such a mechanism. A simple, aryl radical mechanism is, however, consistent with formation of the biaryls whose formation rates depend on $AnH_2$ concentrations.

**B. Some Other Mechanisms. Impurity-Catalyzed Reactions.** Since An pyrolysis does not exhibit an induction period, if the reaction mechanism involves foreign species, these species must act as catalytic agents, not as initiators. The involvement of such agents in our noncatalyzed reactions seems unlikely since results are reproducible and independent of experimental conditions and catalyzed reactions show different kinetic behavior than noncatalyzed reactions.

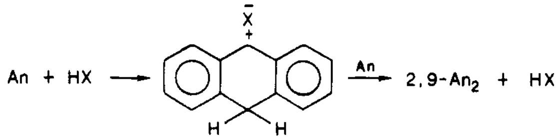
**Triplet-State Intermediates.** A mechanism involving excited (triplet) anthracene, $An^3$, is energetically feasible (triplet energy is 42 kcal $mol^{-1}$ [23]). In fact, electronically excited species have occasionally been suggested as intermediates in aromatic pyrolysis reactions. The following path would yield the observed second-order kinetics

$$\mathrm{An} \underset{k_{\mathrm{isc}}}{\overset{\mathrm{fast}}{\rightleftharpoons}} \mathrm{An}^3 \qquad (6)$$

$$\mathrm{An}^3 + \mathrm{Ar} \xrightarrow[\mathrm{rls}]{k_{\mathrm{add}}} \xrightarrow{-2\mathrm{H}} \mathrm{An\text{-}Ar}$$

where "isc" denotes intersystem crossing and "rls" denotes rate limiting step. Since the equilibrium constant for reaction 6 is 3 $\exp\{-21\,100/T\}$, to match experiment it would be necessary for $k_{\mathrm{add}} = 10^{6.9} \exp\{-1420/T\}$ or $10^{6.0}$ $M^{-1}\ s^{-1}$ at 440 °C. There are two problems with this requirement. First, we can find no precedent for such a rapid, irreversible reaction of a relatively stable triplet species such as $An^3$. Even more serious, to yield second-order kinetics, it is necessary that $k_{\mathrm{isc}} > k_{\mathrm{add}}[\mathrm{An}] \sim 10^{6.7}$ $s^{-1}$. Related intersystem crossing reactions are generally orders of magnitude slower.[24]

**Polarized Intermediates.** The involvement of ions or highly polarized intermediates in this reaction can be excluded on the basis of the low dielectric constant of aromatic solvents at high temperatures, the high endothermicity of ion formation,[25] and the observed independence of rate constant on phase. However, it is likely that halogen-catalyzed polymerization proceeds through polarized intermediates, possibly as shown below



In view of the comparable catalytic activity found for I, Br, and Cl and the large differences in the strengths of their covalent bonds with hydrogen and carbon, one can rule out neutral free-radical processes. Related ionic reactions have been proposed by Buchanen et al. to account for $SbCl_3$-catalyzed pyrolysis of polyaromatic hydrocarbons.[11,12]

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(20) Griffith, L. L.; Billmers, R.; Stein, S. E. *J. Phys. Chem.* **1986**, *90*, 51.

(21) (a) Dickerman, S. E.; Feigenbaum, W. M.; Milstein, N.; Vermont, V. B.; Zimmerman, I.; McOmie, J. F. W. *J. Am. Chem. Soc.* **1973**, *95*, 4624. (b) Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609. (c) Poutsma, M. L. In *Free Radicals*; Kochi, J. K., Ed.; Wiley and Sons: New York, 1973; Vol. I.

(22) Louw, R.; Lucas, H. J. *Recl. Trav. Chem. Pays-Bas* **1973**, *92*, 55.

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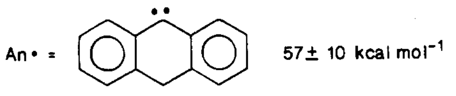
(24) Siebrand, W. *J. Chem. Phys.* **1967**, *47*, 2411.

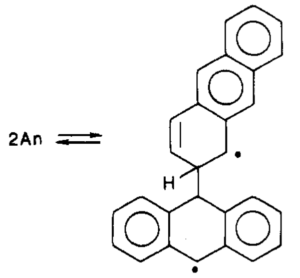
(25) Mautner, M. *J. Phys. Chem.* **1980**, *84*, 2716.

**Carbenes.** Carbenes appear to be too high in energy to be of significance

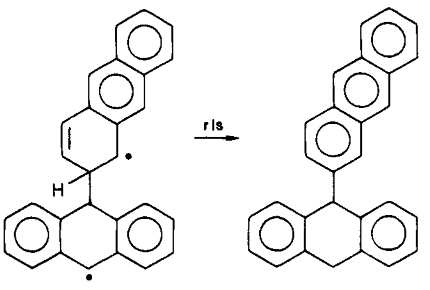


This estimate is based on a 100 kcal/mol Ċ–H bond strength in AnH.

**C. Proposed Mechanism: Biradical Intermediates.** The most direct path leading to 2,9-$An_2$ involves coupling of two ground-state An molecules. We propose this as the actual mechanism with the rate-limiting step being an H-atom transfer within the adduct biradical, as illustrated in reactions 7 and 8. The occurrence of H-transfer in the rls is supported by observed kinetic isotope effects. In addition, redissociation to two ground-state An molecules, the reverse of step 7, is highly exothermic and is likely to be more rapid than the H-transfer step, reaction 8, which involves a substantial negative activation entropy and possibly some strain energy.



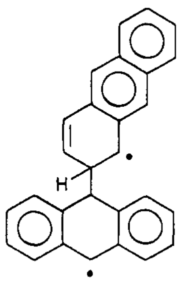
(7)



(8)

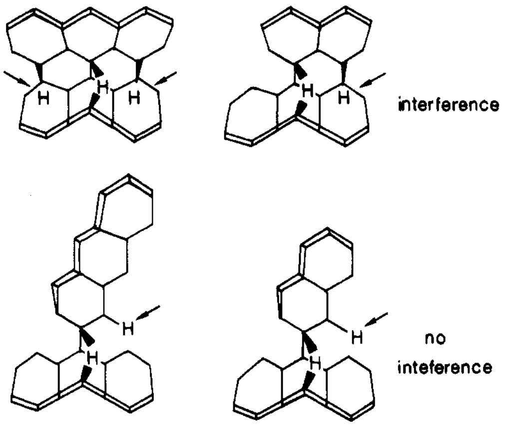
The dihydrobiaryl intermediate formed would have a short lifetime under conditions where it is formed (<5 s at 440 °C, neat An[18]). While a trace dimeric product with the proper mass for such an intermediate molecule was actually observed at very low extents of reaction in the liquid phase (see $An_2H_2$ in Table I).

The above scheme implies that the proposed biradical intermediate



is in equilibrium with two ground-state An molecules. This allows us to equate the observed rate constant, $k_{2,9}$, with the quantity $K_7k_8$. Estimating that $K_7/\text{M}^{-1}\ \text{s}^{-1} = 10^{-4.8}\ \exp\{-17\,300/T\}$, we predict, $k_8/\text{M}^{-1}\ \text{s}^{-1} = 10^{12.2}\ \exp\{-5200/T\}$, a not unreasonable value for such a unimolecular reaction. The proposed biradical intermediate is energetically feasible.

The preference for joining the 9-position of an anthracene molecule with the 2-position of a naphthalene or a second anthracene molecule appears to be a result of steric interference in the paths leading to other 9-substituted isomers. These interferences likely take place in the transition state for the H-transfer and involve interaction between H-atoms on the H-donating molecule and outer rings of the H-accepting (anthracene) molecule. The path joining the 9-anthracene site with the 2-position of an attacking molecule does not involve such interference. These ideas are based on space-filling models and are illustrated below.



The near absence of non-9-substituted biaryls at low reaction extents in neat An is presumably due to the relative instability of their precursor biradicals.

The above scheme can qualitatively account for the observation that adducts (biaryls) of An with relatively unreactive polyaromatic molecules are formed nearly as readily as 2,9-$An_2$. For steric reasons, the 9-An position most readily attaches to the least reactive (2-) An position. This position is not vastly different in reactivity from similar positions in naphthalene, phenanthrene, or biphenyl.[21a] Hence, biaryl formation rates are also not expected to be vastly different.

This scheme is also consistent with observed kinetic isotope effects. These indicate that H-(D-)transfer is involved in the rate-limiting step and that in the An/Np reaction, transfer is from naphthalene to anthracene.

**D. Comparison to Earlier Work.** In terms of decomposition rates, our results are in good agreement with those of Walker et al.[8] based on An disappearance rates. Moreover, the large negative volume of activation reported in their work is consistent with our mechanism, since the increase in density with increasing applied pressure would increase the stability (concentration) of our proposed tight transition state for reaction 8.

Our major product, 2,9-$An_2$, however, has not previously been reported in noncatalyzed reactions. Earlier workers[6,7] reported 2,2-$An_2$ as the major biaryl product. It is possible that at very high extents of reaction, 2,2-$An_2$ might become a major biaryl product since it is the only one incapable of ring condensation. However, we were not able to create conditions where large amounts of it were formed. Moreover, we could not isolate a peak that had the UV spectrum reported for 2,2-$An_2$ (see Experimental Section).

**E. Implications.** In the absence of facile free-radical pathways, polyaromatic molecules can react through more direct paths. The ability of anthracene to form relatively stable reaction intermediates opens up the direct coupling reaction path reported here, a path that dominates over a wide range of temperatures and concentrations.

While it is likely that related reactions play a role in the pyrolysis of other polyaromatic molecules, we hesitate in proposing them as very general means of biaryl formation. Substituents, for example, can open other reaction paths, as observed in the case of naphthol pyrolysis,[26a] where selective biaryl-forming reactions take place by an as yet undetermined mechanism. In benzene pyrolysis, the relative stability of the aromatic nucleus apparently disfavors direct coupling reactions in favor of pathways involving phenyl radicals.[22]

In reaction systems without efficient alternative pathways, direct coupling processes can become important. In condensed-phase carbonization processes, particularly in the later stages where few weak bonds and little free hydrogen is available to facilitate free-radical processes, these reactions may play a major role in cross-linking, aromatization, and graphitization.

Our studies also show that the presence of even trace amounts of halogen atoms can sharply catalyze polyaromatic pyrolysis reactions. While products of these reactions are similar to those of noncatalyzed reactions, kinetics and mechanisms appear to be different.

## Experimental Section

**A. Procedure.** Most condensed-phase pyrolyses were done in evacuated, sealed Pyrex tubes containing 120 ± 25 mg of An. After loading, a rod was sealed into the tube to minimize vapor volume, which was generally less than 10% of the total sample volume. Tubes were heated in a fluidized bath. Gas-phase reactions were performed in a similar manner except only several milligrams of reactant was used.

In several cases, condensed-phase reactions were done in $^1/_8$ in. i.d. gold tubes. These tubes were placed inside Pyrex tubes which were evaluated and sealed prior to immersion in the bath. Several other pyrolyses were done in heat-treated $^1/_4$ in. i.d. stainless steel tubes sealed at both ends by Swagelock[14] fittings.

On the basis of previous studies of bond homolysis rates, the time required to heat the sample to 2° of the final temperature is estimated as 20 s.[15,27]

Several pyrolysis runs were done in Pyrex break-seal tubes in order to measure amounts of evolved noncondensible gas. After pyrolysis these tubes were held at liquid $N_2$ temperatures and then broken under vacuum. Pressures were measured in a calibrated volume with a capacitance manometer.

**B. Analytical Equipment.** A Hewlett-Packard Model 5880 automated capillary GC[14] with FID detection was used for most quantitative analyses. Calibration mixtures were routinely analyzed. Mass spectra of products eluting from the GC were obtained with a HP mass selective detector.[14]

Reverse-phase HPLC with UV absorbance and fluorescence detection was used to analyze a number of product mixtures. Normal-phase HPLC analyses were done on an amino column with gradient elution from pure hexane to pure tetrahydrofuran (THF). Other analyses were done on a gel permeation column with UV detection with THF as a carrier solvent.

**C. Materials.** Most chemicals were obtained from commercial sources and purified by recrystallization. 9,9′-Bianthracenyl was synthesized according to the published methods[28] and identified by GC/MS, melting point, and its complex UV spectrum.

**D. Quantitative Analysis.** All substances detected by GC were assumed to have the same intrinsic FID response factors per C-atom. This was confirmed for the $AnH_2$/An pair to within 3% over the range of concentrations encountered in our experiments. Bianthracenyl products (mostly 2,9-$An_2$ and some 1,9-$An_2$) isolated by TLC and weighed had an average response factor of 0.95 relative to 9,9-$An_2$. In view of possible uncertainties of at least 5% in this value, we assume that this value is actually unity.

**E. Product Identification.** Product structures were determined by a combination of UV analysis of LC peaks, capillary GC/MS, retention time considerations, and, in some cases, by GC coinjection. Relative retention times and peak areas of dimeric products in GC and reversed-phase HPLC analysis were very similar, so that identities of GC and LC peaks could be easily connected. This was confirmed by GC injection of the 2,9-$An_2$ and 1,9-$An_2$ peaks collected by HPLC.

Products 9,9-$An_2$ and 2,9-$An_2$ were identified by precise matching of their complex UV spectra with available spectra.[29] The identity of 9,9-$An_2$ was further confirmed by coinjection. $AnH_2$ was identified by GC/MS and coinjection.

There are six possible dianthracenyl isomers and exactly six peaks were observed with parent masses corresponding to dianthracenes ($m/e$ = 354). With the possible exception of 2,2-$An_2$ (see below), these peaks were all well resolved; typical retention times (min) and assigned structures (see below for rationale) are 20.8 (9,9-$An_2$); 22.3 (1,9-$An_2$); 24.0 (1,1-$An_2$); 27.2 (2,9-$An_2$); 29.0 (1,2-$An_2$); 37.6 (2,2-$An_2$).

These assignments were made by using the known 9,9-$An_2$ and 2,9-$An_2$ peaks along with the idea that relative retention times increase with decreasing steric interference (or with increasing molecular "surface area"). That is, retention times increase in the order 9 < 1 < 2 substitution. For instance, the three isomeric binaphthalenyls eluted in the order 1,1′ < 1,2′ < 2,2′ with retention times of 8, 9, and 10 min. Therefore, the two bianthracenyl peaks eluting between 9,9-$An_2$ and 2,9-$An_2$ were assigned to 1,9-$An_2$ and 1,1-$An_2$, the peak just after 2,9-$An_2$ to 1,2-$An_2$, and the peak eluting well after 1,2-$An_2$ to 2,2-$An_2$.

To confirm the identity of the major diaryls, they were generated by the pyrolysis of anthracene aldehydes in the presence of a fivefold excess of anthracene or naphthalene (440 °C in the gas phase). Under these conditions aryl aldehydes are efficient sources of aryl radicals. A mixture of benzaldehyde and biphenyl, for example, generated the three terphenyl isomers, while benzaldehyde and naphthalene gave the two phenylnaphthalene isomers. In addition, 1- and 2-naphthaldehyde in naphthalene gave the expected dinaphthalenyls (the former gave only the 1,1′ and 1,2′ isomers, the latter gave the 1,2′- and 2,2′-binaphthalenyls). Further, for the phenyl radical case, ratios of isomeric products were the same as in reaction systems containing a clear-cut phenyl radical initiator, diphenyl diketone (PhCOCOPh), in place of benzaldehyde. A series of detailed studies of these arylation reactions are under way in our lab.

In the 9-anthraldehyde/anthracene reaction, only three bianthracenyls were observed. They corresponded to the products of the anthracene pyrolysis reaction ascribed to 9,9-$An_2$, 1,9-$An_2$, and 2,9-$An_2$ (relative amounts were 1:0.4:0.4). In the 1-anthraldehyde/anthracene reaction, products matched those of 1,9-$An_2$, 1,1-$An_2$, and 1,2-$An_2$ (1:0.15:0.15). In the 9-anthraldehyde/naphthalene reaction two major cross-biaryls were detected and found to precisely match in retention time the cross-biaryls in anthracene/naphthalene pyrolysis. In view of these retention times the earlier peak was identified as 1-naphthyl-9-anthracene and the later as 2-naphthyl-9-anthracene. There was one surprise from these runs. The peak maxima in our UV spectrum of 1,1-$An_2$ did not match literature data for this compound.[7] However, the spectrum of 1,9-$An_2$ did match this spectrum. Apparently, the previous attempted synthesis of 1,1-$An_2$[7] actually generated 1,9-$An_2$.

Some uncertainty remains concerning the identity of 2,2-$An_2$. No collected LC peak had a UV spectrum even roughly similar to the literature spectrum.[6,7]

At very low extents of reaction a product of mass 258 ($An_2H_2$) eluting between 1,1-$An_2$ and 2,9-$An_2$ was observed by GC. Over the range of decomposition 0.01% to 0.1% the area of this peak relative to 2,9-$An_2$ remained roughly constant at 0.2, so this substance did not behave as expected for a simple precursor of 2,9-$An_2$. Its relative concentration declined sharply above ~0.2% overall decomposition. Too little of this product was formed for isolation or UV analysis.

Several secondary reaction products were observed once the decomposition extent exceeded ~5%. One product eluted between An and $AnH_2$ had mass 182 and was presumably 1,2,3,4-tetrahydroanthracene. It also became a noticeable product in experiments where $AnH_2$ was added to the reaction mixture.

Two major condensed dimeric products eluting after the bianthracene were detected by GC/MS and LC. They were iden-

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tified by their parent masses of 352 and their UV spectra[30] as the two isomeric benzonaphthofluoroanthenes (I and II, see earlier). These same products were also reported in the $SbCl_3$-catalyzed pyrolysis of An[11,12] and are the expected condensation products of the major dimer, 2,9-$An_2$.

Gel permeation chromatography of pyrolysis mixtures from reaction at 440 °C for 1 h showed two well-defined peaks corresponding to the dianthracenes and to An. Only a very small peak was observed before the rather sudden onset of the dimer peak, suggesting the near absence of trimeric and larger products.

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**Registry No.** An, 120-12-7; $AnH_2$, 613-31-0; 2,9-$An_2$, 67263-10-9; 1,9-$An_2$, 1055-23-8; naphthalene, 91-20-3; phenanthrene, 85-01-8; biphenyl, 92-52-4; diphenyl ether, 101-84-8.

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# The Question of Friedel–Crafts Transformylations. Acid-Catalyzed Reactions of Aromatic Aldehydes with Arenes

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The reactions of aromatic aldehydes with various arenes in the presence of Lewis and Brønsted acids have been examined with the aim of determining if transformylations occur. No evidence for such transformylations was obtained. The major initial reaction is nucleophilic addition of the arene to the carbonyl group of the aldehyde to produce a diarylmethanol, followed by reaction with a second molecule of arene with elimination of water to produce a triarylmethane. Further reactions include (1) reversible dealkylations/realkylations of triarylmethanes to yield di- and triarylmethanes having aromatic nuclei corresponding to those of both the initial aldehyde and the arene and (2) alkylation, cyclialkylation, and dealkylation reactions that result in the formation of anthracene and/or substituted anthracenes and dihydroanthracenes. The anthracene and dihydroanthracene derivatives are produced in significant amounts only when aluminum chloride is the acid catalyst. The mechanisms of the reactions of aromatic aldehydes with arenes in the presence of aluminum chloride are discussed and compared with reactions of aromatic ketones.

In previous papers[1,2] we have described the occurrence of certain Friedel–Crafts transacylations and transsulfonylations. The results of these investigations led us to consider the possibility of analogous transformylations—reactions of aromatic aldehydes with nucleophilic arenes that result in the transfer of a formyl group from one aromatic nucleus to another. Although the reactions of aromatic ketones and sulfones with arenes in the presence of Lewis and protonic acids had not received much attention until recently, the analogous reactions of aldehydes have been investigated rather extensively. The addition of benzene to benzaldehyde in the presence of $AlCl_3$ or $FeCl_3$ was reported by Schaarschmidt et al.[3] to give triphenylmethane and anthracene. Further work by Hey[4] and Ungnade[5] showed that substituted triphenylmethanes and anthracenes were formed by the reactions of other aromatic aldehydes with aromatic hydrocarbons such as toluene and xylenes in the presence of excess $AlCl_3$. For example, reaction of *p*-tolualdehyde with benzene in the presence of $AlCl_3$ gave triphenylmethane, anthracene, and toluene.[4a] The results of these studies were interpreted as indicating that the aldehyde provides the meso carbons of the anthracene molecules and the methinyl carbon of the triphenylmethane molecules, whereas the hydrocarbon rings supply the two end rings of the anthracene molecules and the three rings in the triphenylmethane molecules.

The initial step in these reactions was considered by Hey and Ungnade to be the decarbonylation of the aldehyde, the reverse of a Gattermann–Koch reaction,[6,7] rather than a transformylation. The aldehyde expected from a transformylation reaction was never detected. The carbon monoxide produced by the decarbonylation was presumed to react with the aromatic hydrocarbons in some unspecified way to produce the triarylmethanes and anthracenes.

In view of the transacylations and transsulfonylations that we had recently observed, it became of interest to us to investigate the possibility that transformylations may actually occur in the reactions of aromatic aldehydes of the types described by Hey and Ungnade and that the aldehyde produced by transformylation may be an intermediate in these reactions although it has gone undetected. The present work was designed to determine whether or not such a transformylation may occur, with the hope that

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