stable to the hydride/distillation, were stirred over 4-Å molecular sieves, sparged with nitrogen, and stored under nitrogen. The alkanes used as internal standards were obtained from the Humphrey Chemical Co. and were used as received. A solution of 9-BBN in THF was made and standardized prior to use according to the literature procedure.[11d]

Instruments. The GC analyses were carried out on a Hewlett-Packard 5790A gas chromatograph equipped with a flame ionization detector and 3.2-mm-o.d. columns. The chromatograph was connected to a Hewlett-Packard 3390A integrator for determining peak areas. The following GC columns were used: 4 m of 10% SE-30 on 100/120-mesh Chromosorb W; 6 m of 10% Carbowax 20M on 100/120-mesh Chromosorb W; 2 m of OV-17 on 100/120-mesh Chromosorb W. The GC/MS spectra were obtained on a Hewlett-Packard 5985 gas chromatograph/mass spectrometer/data system equipped with 2 m of a 3.2-mm-o.d. column packed with 3% SE-30 on 100/120-mesh Chromosorb W.

Oxymercuration. Reversibility of Oxymercuration. Since oxymercuration can be reversible under the conditions employed here, it was necessary to ascertain the irreversiblity of a reaction before it could be used in a competitive study. Irreversiblity had been established for the nonfunctionalized alkenes,[9] 3-chloropropene,[5f] vinyltrimethylsilane,[5d] and 3-methoxypropene.[5e]

The relative reactivities of the alkenes were determined by competitive reactions, using the following typical procedure:[9] 10 mmol each of two olefins was introduced into 50 mL of 80% aqueous THF. The solution was cooled to 0 °C. Then, 10 mmol of mercuric acetate was added to the stirred solution. After the solution was stirred for a sufficient time to ensure complete reaction, 10 mL of 0.5 M sodium hydroxide was added followed by 10 mL of 0.5 M sodium borohydride in 3 N sodium hydroxide. A suitable internal standard was added. After the precipitated mercury had coagulated, the aqueous phase was saturated with sodium chloride and potassium carbonate, and the organic layer was analyzed for residual alkenes. In all cases, the total equivalents of alkenes consumed was consistent with the equivalents of $Hg(OAc)_2$ used. The alkene pairs studied by competitive oxymercuration include the following: 3-chloropropene/2-methyl-1-pentene, 3-chloropropene/3,3-dimethyl-1-butene, vinyltrimethylsilane/cyclohexene, 3-methoxypropene/cyclohexene.

Hydroboration. Irreversibility of Hydroboration. The irreversibility of hydroboration under the conditions employed here has been established.[11]

Competitive Reactions. The relative reactivities of the alkenes were determined by competitive reactions, which were carried out as follows:[8] A total of 10 mL of THF was injected into a flask, which had been baked at 140 °C for 24 h, cooled under a flow of nitrogen, and equipped with an adapter and a magnetic stirring bar. A total of 1 equiv (5 mmol) of each of the two alkenes to be compared was added via syringe. Then 0.5 equiv (2.5 mmol) of an *n*-alkane was added as an internal standard. After a small amount of the solution (1 μL) was removed for analysis, 1 equiv of 9-BBN (5 mmol) in THF solution was injected. The temperature was maintained at 25 °C, and the solution, stirred for 24 h. The contents of the flask were then analyzed by GC to determine the amounts of the residual alkenes. In all cases, the total equivalents of alkenes consumed were consistent with the equivalents of 9-BBN employed. The alkene pairs thus studied include the following: 1-hexene/3-(trimethylsilyl)propene, 1-hexene/2-propenylethanoate, 3,3-dimethyl-1-butene/2-propenylethanoate, 1-hexene/3-(methylthio)propene, 3,3-dimethyl-1-butene/3-(methylthio)propene, 1-hexene/3-methoxypropene, 3,3-dimethyl-2-butene/3-methoxypropene, 1-hexene/3-butenenitrile, 2-methyl-2-butene/3-butenenitrile, cyclopentene/3-butenenitrile, 3,3-dimethyl-1-butene/3-butenenitrile, 1-octene/vinyl acetate, 1-octene/vinyltrimethylsilane, 1-hexene/vinyl phenyl sulfide, 2-methyl-2-butene/vinyl phenyl sulfide, 1-octene/vinyl butyl ether, 2-methyl-1-pentene/vinyl butyl ether, 2,3-dimethyl-1-butene/*trans*-1-bromo-1-butene, cyclohexene/*trans*-1-bromo-1-butene, 1-chloro-2-methylpropene/2,3-dimethyl-2-butene.

Regioselectivity in Hydroboration of 3-(Methylthio)propene. Hydroboration of 3-(methylthio)propene (5 mmol) with 9-BBN was performed as above, and after it was stirred overnight, the contents were oxidized with 1.83 mL of 3 N sodium hydroxide and 1.63 mL of H_2O_2 (31%) solution. After the solution was stirred for 1 h, the aqueous layer was saturated with sodium chloride and the THF layer separated and dried over anhydrous $MgSO_4$. The GC/MS of the solution was run, and the peaks were identified and weighed. The ratio of 3-(methylthio)propan-1-ol to 3-(methylthio)propan-2-ol was found to be 97.6 to 2.4.

Calculation of Relative Reactivities. For maximum precision, the relative reactivity of alkenes in each pair compared should be less than 7. If it is greater, the residual amounts of the two alkenes differ greatly, and there will be an undesirably high error in the measurement of the alkene present in lower concentration. Therefore, an initial value of the reactivity of each functionalized alkene was determined through a competitive reaction with 1-hexene. If this number was greater than 7, it was refined by carrying out a competitive reaction of the functionalized alkene with another alkene having a similar, previously determined reactivity. In these cases, internal consistency of the relative reactivities was expected and observed. The relative rates were calculated according to the Ingold–Shaw equation.[20] Each reaction was run in triplicate, and the average is reported.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We also appreciate the support of the Research Corp. and the National Science Foundation.

Registry No. 1, 111-34-2; **2**, 762-72-1; **3**, 763-29-1; **4**, 592-41-6; **5**, 627-40-7; **6**, 10152-76-8; **7**, 108-05-4; **8**, 754-05-2; **9**, 591-87-7; **10**, 556-56-9; **11**, 109-75-1; **12**, 106-95-6; **13**, 107-05-1; **14**, 1822-73-7; **15**, 513-35-9; **16**, 7642-09-3; **17**, 13269-52-8; **18**, 590-18-1; **19**, 32620-08-9; **20**, 7611-87-2; **21**, 563-79-1; **22**, 116504-05-3; **23**, 116504-06-4; **24**, 513-37-1; **25**, 69322-51-6; 9-BBN, 280-64-8; $Hg(OAc)_2$, 1600-27-7; $H_2C{=}CHCH_2BMe_2$, 44389-67-5; $H_2C{=}CHCH_2NMe_2$, 2155-94-4.

Reactivity of Polycyclic Aromatic Aryl Radicals

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Received November 23, 1987. Revised Manuscript Received July 1, 1988

Abstract: Results of experimental and theoretical studies of the properties and reactions of polycyclic aromatic aryl radicals are reported. Reactions of phenyl, 1- and 2-naphthalenyl, and 9-anthracenyl radicals with toluene and naphthalene were examined in the gas phase at 400 and 450 °C. Arylation rates for each radical were measured relative to hydrogen abstraction from toluene (k_{ar}/k_{abs}). For reactions with toluene of both phenyl and 2-naphthalenyl radicals, this ratio was 0.20–0.25. For the 1-naphthalenyl and 9-anthracenyl radicals, these ratios were signficantly lower (0.05 and 0.01, respectively). Relative rates for arylating the different available positions in toluene and naphthalene, however, were not nearly as different. Differences in arylation/abstraction rates of the different radicals are explained in terms of differing degrees of reversibility for the initial addition step. Results are consistent with literature dissociation rate constants measured by Ladaki and Szwarc for aryl bromides. MNDO calculations on a range of arene–aryl radical pairs suggest that these differences originate primarily from differences in radical stabilities. Calculations also suggest that, on the basis of bond strengths, aryl radicals can be roughly divided into three groups, which depend on the nature of the two neighboring aromatic carbon atoms and are independent of the size of the aromatic cluster.

A wealth of information on the reactivity of phenyl and substituted phenyl radicals is available.[1-8] Their ubiquity, relative ease of generation, and high reactivity are responsible for the large number of studies in this area. However, there exist little data

Table I. Reactions of Aryl Radicals with Toluene and Toluene-d_8[a]

radical	substrate	no. of runs	relative arylation rate				abstraction/ arylation[b]
			ipso(methyl)	ortho	meta	para	
phenyl	toluene	17	0.45 ± 0.04	0.57 ± 0.02	1	1.17 ± 0.17	5.21 ± 0.49
	toluene-d_8	25	0.92 ± 0.05	0.53 ± 0.03	1	1.12 ± 0.08	5.23 ± 0.09
1-naphthalenyl	toluene	47	0.15 ± 0.02	0.90 ± 0.06	1	1.17 ± 0.08	21.08 ± 3.81
	toluene-d_8	13	0.33 ± 0.04	0.90 ± 0.06	1	1.16 ± 0.08	20.65 ± 3.47
2-naphthalenyl	toluene	51	0.36 ± 0.07	0.61 ± 0.04	1	1.18 ± 0.09	4.13 ± 0.57
	toluene-d_8	10	0.84 ± 0.08	0.53 ± 0.04	1	1.11 ± 0.09	3.92 ± 0.36
9-anthracenyl	toluene	37	*c*	0.60 ± 0.04	1	0.91 ± 0.07	93.43 ± 12.92
	toluene-d_8	8	0.18 ± 0.02	0.60 ± 0.07	1	0.93 ± 0.03	88.07 ± 12.30

[a] The reactions were carried out at 400 and 450 °C, and the average value was calculated. Within experimental uncertainty, results at these two temperatures were the same. Reaction times varied from 5 to 60 min with no systematic variations in rates. Relative rates were also unaffected by the addition of ca. 5% bibenzyl (see text). [b] Ratio of arene to the sum of the arylated products. [c] Unable to obtain an accurate value due to the small amount formed.

on the reactivity of aryl radicals derived from polynuclear aromatic hydrocarbons (PAH). Such species are also ubiquitous, especially as intermediates in the pyrolysis of aromatic compounds[9,10] and as potential reactive sites in the reactions of carbonaceous materials. They are also of interest at a more fundamental level, since possible unidentified $\sigma-\pi$ interactions might significantly influence their reactivity.[11] We have conducted a series of experimental and theoretical studies on these radicals to clarify their reactive properties. We report experimental studies of the reactions of phenyl, 1-naphthalenyl, 2-naphthalenyl, and 9-anthracenyl radicals with toluene and naphthalene. Arylation rates for each radical were determined relative to H abstraction from toluene. To assist in the analysis and generalization of results, theoretical studies applied the MNDO method to these and a number of other 3-, 4-, and 5-ring benzenoid aryl radicals.

Methods

Experimental Method. All chemicals were obtained from commercial sources and, in most cases, purified by recrystallization or distillation before use. Toluene, the major component of most mixtures, was obtained from Aldrich Chemical Co. (99.9% Gold Label) and was used without purification.

Reactions were done in sealed, evacuated Pyrex ampules under conditions where reactions took place in the gas phase. In a typical experiment a 1-cm^3 tube contained 2–20 mg of a 1–10% solution of an aryl aldehyde in toluene. In some experiments 1–2% bibenzyl (1,2-diphenylethane) was added as a free-radical initiator. The tubes were heated in a fluidized bath at 400 or 450 °C. No measurable differences in product distribution were observed at these two temperatures. After reaction, products were frozen into the bottom of the tube and dissolved in a low-boiling solvent (carbon disulfide or methylene chloride).

Reaction mixtures were analyzed by capillary gas chromatography with a 50-m cross-linked methyl silicone fused silica column. Peak areas from a flame-ionization detector gave relative concentrations. Calibration runs for the phenyl aromatics and methylbiphenyls showed, as expected, that this was a valid assumption. All phenyl aromatics, methylbiphenyls, and binaphthyls were identified by coinjection with authentic samples. Other arylated products were identified by GC/MS and relative retention times. Elution times of products from the arylation of toluene were assumed to fall in the order found for phenylation,[12] namely, ortho ≪ meta < para, and arylation products of naphthalene in the order 1-substitution < 2-substitution. Relative retention times and peak areas of the arylated products were virtually identical for each of the aryl radicals.

Computational Method. All calculations reported here were done with the MNDO method of Dewar and Thiel.[13] All geometrical parameters were allowed to vary during the optimization process, and planarity was assumed. Aryl radical calculations used the half-electron (HE) option.[14]

The use of MNDO to calculate the electronic and thermodynamic properties of organic compounds was recently reviewed by Clark.[15] MNDO was found to be useful for computing the electronic and thermodynamic properties of hydrocarbons. This, combined with the fact that most of the species of interest were too large to treat by reliable ab initio procedures, led us to rely on MNDO for our investigation.

Results

Experimental Results. Aryl radicals, Ar$^\bullet$, were generated by the free-radical-induced dissociation of aryl aldehydes, ArCHO. Closely related thermal reactions of aldehydes are well documented in the literature.[16] Reaction mixtures contained a small amount of aryl aldehyde, an excess of toluene (or *p*-xylene), and in some cases naphthalene. Typical extents of aldehyde decomposition at 450 °C for 30 min are the following: benzaldehyde, 10%; 1-naphthaldehyde, 16%; 2-naphthaldehyde 10%; 9-anthraldehyde, 70%.

The mechanism for reaction of an aldehyde in the presence of toluene is shown in eq 1–6. In the presence of added naphthalene, products of arylation at the 1- and 2-positions of naphthalene were also observed (eq 7 and 8).

Typical concentrations of the aldehydes were the following: benzaldehyde, 5%; 1- and 2-naphthaldehyde, 2%; 9-anthraldehyde, 1%. These were sufficiently low to ensure that significant abstraction by the aryl radicals from the aldehydes did not occur. This was verified in labeling experiments using toluene-d_8 in place of nondeuteriated toluene, where >90% of the product arenes contained a single D atom (abstraction from the aldehyde would have led to nondeuteriated arenes). In addition, relative abstraction/arylation rates, as measured by relative amounts of product arenes to arylated products, did not depend on aldehyde concentration over the ranges of concentration used in this work. Aryl abstraction from the parent aldehyde only became apparent at relative concentrations of aldehydes to toluene 5–10 times greater than those given above, at which point a distinct increase in arene products relative to arylated products was observed.

Results of studies of aryl radicals with toluene and toluene-d_8 are given in Table I. For phenyl radicals, these rates were virtually identical with those obtained in similar studies with diphenyldiketone as the radical source.[17]

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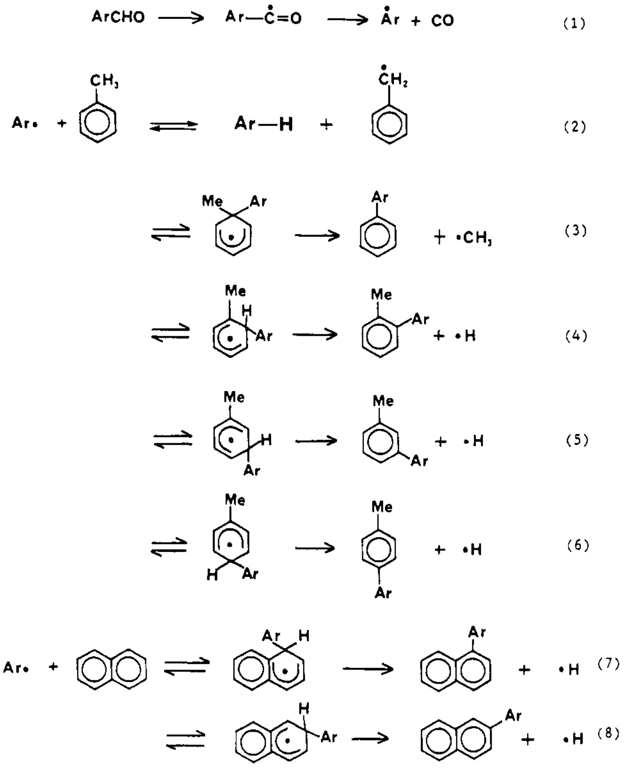

As a test of the above mechanism, 1–2% bibenzyl, a radical initiator, was added to the reaction mixture for each aldehyde. It increased the dissociation rates by roughly a factor of 10 but had no measurable effect on the observed relative rates of aryl radical reactions.

Results of the reactions of aryl radicals with naphthalene are given in Table II.

A single side product resulting from the net displacement of the aldehyde group by a benzyl group was observed in each reaction. These presumably were formed in a reaction of the aryl aldehyde with benzyl radicals. The products observed when toluene-d_8 or *p*-xylene replaced toluene supported this idea. Concentrations of these side products depended strongly on the nature of the aldehyde. As a percentage of detected products of the aldehyde, these products were approximately 0.8% for benzaldehyde, 2% for 2-naphthaldehyde, 5% for 1-naphthaldehyde, and 50% for 9-anthraldehyde. These relative amounts are in qualitative accord with relative rates expected for attack at the substituted position in the aldehydes.

Small amounts of 9,10-dihydroanthracene (<10% the anthracene product) were observed in the 9-anthraldehyde reaction. No other significant side products could be observed in any reaction.

With 1–2% added bibenzyl, extents of reaction were high enough at 450 °C (30–50% at 5–15 min) to obtain meaningful mass balances with toluene as an internal standard. These were the following: benzaldehyde, 0.92 (one run); 1-naphthaldehyde, 1.02 ± 0.8 (three runs); 2-naphthaldehyde, 1.05 ± 0.10 (two runs); 9-anthraldehyde (0.98 ± 0.04). In the cases of 9-anthraldehyde, where extents of reaction were high in the absence of added bibenzyl, we obtained a mass balance of 0.98 ± 0.04 (two runs).

The homogeneity of the principal reactions were supported by the following observations: (1) similar results for two phenyl radical sources; (2) reproducibility of results; (3) known high reactivity of phenyl and high pressure; (4) increase in rate of overall reaction without change in product distribution upon adding a radical initiator (bibenzyl).

Theoretical Results. The polycyclic aromatic structures studied in this work by MNDO are shown in Figure 1. Aryl radicals, which were derived from these molecules by cleaving the C–H bond at the numbered positions in this figure, were also studied.

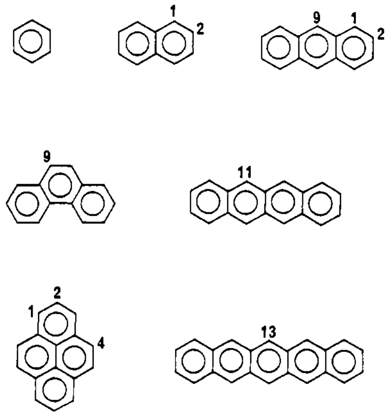

Figure 1. Polycyclic aromatic structure studied in this work by MNDO. The numbered positions denote the C–H bonds that are cleaved.

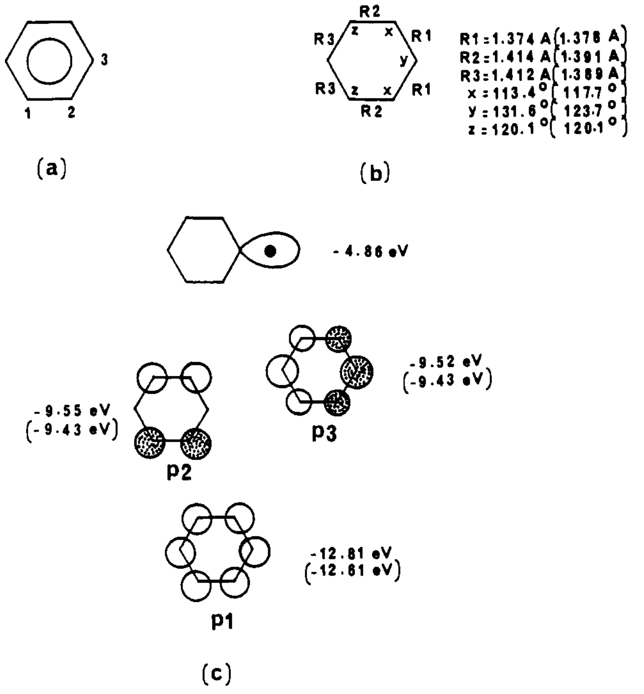

Figure 2. Key: (a) benzene; (b) optimum MNDO and ab initio (in parentheses), geometry of phenyl radical; (c) shapes and MNDO energies of the three π MOs (P1–P3) and SOMO of phenyl radical. The corresponding MNDO π MOs energies of benzene are given in parentheses.

Table II. Reactions of Aryl Radicals with Naphthalene[a]

radical	no. of runs	$k_{ar,1}$[c] and $k_{ar,2}$	k_{ar}(np)[d] and k_{ar}(toluene)[d]
phenyl	1[b]	0.70	3.67
1-naphthalenyl	18	1.33 ± 0.19	4.69 ± 0.33
2-naphthalenyl	14	0.81 ± 0.07	4.77 ± 0.64
9-anthracenyl	10	1.53 ± 0.25	2.72 ± 0.43

[a] The reactions were carried out at 400 and 450 °C, except where noted, and the average was calculated. [b] This reaction was done at 450 °C only. [c] $k_{ar,1}$ and $k_{ar,2}$ are the rates of naphthalene arylation at positions 1 and 2, respectively. [d] Here, k_{ar}(np) refers to the total rate of arylation of naphthalene (= $k_{ar,1}$ + $k_{ar,2}$).

Table III. Energies (eV) of the SOMOs of Aryl Radicals Relative to Phenyl

radical	(E − E(phenyl))	radical	(E − E(phenyl))
phenyl	0.00	9-phenanthrenyl	−0.03
1-naphthalenyl	0.04	11-tetracenyl	−0.04
2-naphthalenyl	−0.03	1-pyrenyl	0.01
1-anthracenyl	0.02	2-pyrenyl	−0.07
2-anthracenyl	−0.03	4-pyrenyl	0.01
9-anthracenyl	−0.03	13-pentacenyl	−0.08

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Table IV. π MOs Energies (eV) of Pentacene and 13-Pentacenyl Radicals

π MO[a]	pentacene	13-pentacenyl	difference
P1	-13.78	-13.89	0.11
P2	-13.16	-13.21	0.05
P3	-12.29	-12.36	0.07
P4	-11.19	-11.25	0.06
P5	-10.96	-11.06	0.10
P6	-10.44	-10.50	0.06
P7	-10.03	-10.06	0.03
P8	-9.61	-9.66	0.05
P9	-8.84	-8.91	0.07
P10	-8.56	-8.62	0.06
P11	-7.49	-7.50	0.01

[a] P1–P11 denote the lowest to the highest π MO energies.

Table V. MNDO and Experimental Enthalpies of the Formation of the Various Arene–Aryl Systems Studied (All Values in kcal/mol)

arene	MNDO	exptl[a]	aryl	MNDO	exptl[b]
benzene	21.3	19.8	phenyl	78.1	78.6 ± 2
naphthalene	38.3	35.8	1-naphthalenyl	93.9	
anthracene	58.5	54.4	1-anthracenyl	114.2	
			2-anthracenyl	115.5	
			9-anthracenyl	113.2	
phenanthrene	55.7	50.0	9-phenanthrenyl	110.6	
tetracene	80.9	67.8	11-tetracenyl	135.1	
pyrene	60.7	51.6	1-pyrenyl	116.4	
			2-pyrenyl	117.0	
			4-pyrenyl	115.7	
pentacene	103.7		13-pentacenyl	158.0	

[a] Reference 26b. [b] Reference 25a.

The effect on the geometry of such bond breaking is shown in parts a and b of Figure 2 for the benzene–phenyl pair. The associated MO energies shifts in going from benzene to phenyl and pentacene to pentacenyl are given in Figure 2c and Table IV, respectively. The energies of the singly occupied molecular orbitals (SOMO) in all studied radicals are listed in Table III.

The aryl–H bond strengths, calculated from MNDO, of the various arenes shown in Figure 1 are given in Table VI. These were obtained from the difference in MNDO heats of formation of each aryl radical and its parent arene (Table V).

Discussion

Experiment. The aryl radicals differed significantly in their relative arylation/H-abstraction rates (k_{ar}/k_{abs}). Relative to the reaction of phenyl radical with toluene, these ratios were the following: 2-naphthalenyl, 1/1; 1-naphthalenyl, 1/4; 9-anthracenyl, 1/18. Since all of the H-abstraction reactions are highly exothermic and differences in abstraction enthalpy and entropy are not likely to be large, H-abstraction rates for these radicals are expected to be very similar. On this basis, we assume that differences in k_{ar}/k_{abs} are primarily due to differences in arylation rates (k_{ar}).

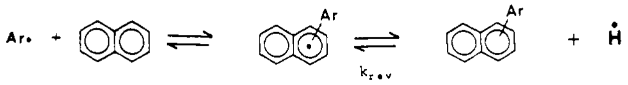
Relative rates of arylation at the different sites were the same within a factor of 2 for each of the aryl radicals. However, these rates were not in the order expected for radical addition rates. For instance, at 80 °C in solution, the relative rate for the addition of a phenyl radical to the 1-site in naphthalene has been reported to be a factor of 4 greater than addition to the 2-site.[1,18a] The higher reactivity of the 1-position of naphthalene is a general finding and is well supported by theory.[19,20] But, in our experiments, for phenyl and 2-naphthalenyl the net rate of 2-arylation was actually greater than 1-arylation. An even more striking case is the phenylation of toluene, where, near room temperature, *o*-phenylation is 3.5 times faster than *m*-phenylation,[1] while in our studies the former reaction is about 2 times *slower* than the latter. These differences are probably a consequence of reversibility at the high temperatures of our experiments. A variety of other experimental evidence also indicates that arylation reactions are reversible at our temperatures.[7,17,18b–c]

Table VI. Experimental and MNDO BDEs of the Various Ar–X Sites (All Values in kcal/mol)

		BDE relative to phenyl-X		
			exptl	
Ar	BDE of Ar–X bond: MNDO (X = H)	MNDO (X = H)	X = H[a]	X = Br[b]
phenyl	108.9	0.0	0.0	0.0
2-naphthalenyl	108.6	-0.3	0.3	-0.6
2-anthracenyl	109.1	0.2		
2-pyrenyl	108.4	-0.5		
1-naphthalenyl	107.7	-1.2	-1.9	-1.1
9-phenanthrenyl	107.0	-1.9		-2.0
1-anthracenyl	107.8	-1.1		
1-pyrenyl	107.8	-1.1		
4-pyrenyl	107.1	-1.8		
9-anthracenyl	106.8	-2.1	-4.0	-5.5
11-tetracenyl	106.3	-2.6		
13-pentacenyl	106.3	-2.6		

[a] From relative arylation/abstraction rates in Table I at the mean experimental temperature of 425 °C. [b] From relative rates of dissociation of aryl bromides.[27]

Assuming that methyl displacement rates are the same in toluene and toluene-d_8, the data in Table I show that H displacement on aromatic carbons is a factor of 2 faster than D displacement. This confirms that H loss is rate limiting and therefore that phenyl addition is reversible. We now examine reversibility in a little more detail.



Assuming reversibility for phenyl addition, it is convenient to express the net arylation rate constant as the product of the rate constant for the hypothetical reverse reaction (H atom addition to the site of arylation, which under the above assumption of phenyl reversibility, is irreversible) and the overall equilibrium constant

$$k_{net} = k_{rev}K_{eq}(\mathrm{Ar}^{\bullet} + \mathrm{Ar'H} = \mathrm{Ar{-}Ar'} + \mathrm{H})$$

This equation, in effect, separates the thermodynamic and kinetic contributions to the observed arylation rate. It shows that relative arylation rates depend directly on differences in reaction energy. We suggest that the reason why arylation at the 2- and 1-positions occurs at comparable rates is that the inherently higher reactivity (that is, higher k_{rev}) of the 1-position is more than compensated for by a lower stability of the final diaryl product (K_{eq} is lower for 1-arylation than for 2-arylation).[1,18a] This requires that 2-arylnaphthalenes are more stable than 1-arylnaphthalenes, a plausible idea considering the steric crowding in the latter.

Differences in relative arylation/H-abstraction rates cannot be treated in the same manner. In these cases, all of the reverse reactions are H additions to phenyl rings; these are not expected to depend significantly on the nature of the arene. We presume that these differences are due primarily to differences in reaction thermochemistry (in K_{eq}), with only minor contributions from differences in reverse-reaction rate constants. Our experimental measurements, however, do not provide information concerning the origin of these thermodynamic differences. That is, are they primarily a consequence of differences in intrinsic radical stabilities or different strain energies in the products (as proposed above to explain the small differences in relative rates for 1- and 2-arylation of naphthalene)?

Thus, phenyl and 2-naphthalenyl radicals form equally strong bonds with arenes, the 1-naphthalenyl radical forms weaker bonds,

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and bonds of the 9-anthracenyl radical are still weaker. Relative to the phenyl radicals, derived Gibbs energies (kcal/mol) of arylation at the mean experimetnal temperature are −0.3 for 2-naphthalenyl, 1.9 for 1-naphthalenyl, and 4.0 for 9-anthracenyl.

In order to assist in the generalization of our experimental findings, we have carried out a number of MO calculations. We were especially interested in determining whether observed trends in radical reactivity could be explained entirely in terms of differences in radical thermodynamic stability and, if so, how these differences could be generalized.

Theory. Electronic Structure of Aryl Radicals. In this section, we discuss our MNDO results on the ground state of a series of benzenoid polycyclic aromatic molecules and free radicals (Figure 1). Differences in electronic properties of these radicals and their parent molecules are examined and compared to earlier studies. Then, predictions concerning the electronic ground state of other aryl radicals are made.

The optimum geometries of the phenyl radical and benzene, as obtained from MNDO, are somewhat different. Specifically, as shown in Figure 2, upon C–H bond cleavage, the bond angle at the radical site (C3) increases from 120.0° to 131.6°. At the same time, C2–C3 and C3–C4 bond lengths are reduced from the benzene value of 1.406–1.374 Å. Angular distortions occur also in other places in the benzene ring, especially at C2 and C4, in order to accommodate the large perturbation at C3. The same qualitative behavior, but with somewhat smaller differences between benzene and phenyl, has been obtained from ab initio calculations[21] and is given in parentheses in Figure 2b.[21a]

As is clear from Figure 2c, the π MOs of the phenyl radical have only slightly different energies than corresponding MOs in benzene; energies are lowered by 0.2, 0.12, and 0.09 eV for P1, P2, and P3, respectively.[22a] The strong bond cleavage perturbation that occurred in the σ framework thus had an "indirect" influence on the π MO energies. This influence must be indirect since the σ and π networks do not overlap. As for the SOMO, it is clear from Figure 2c that it is strongly polarized in the direction of the broken bond and is well localized at the perturbation site. Nearly 84% of its wave function is concentrated at the radical center. In summary, breaking one of the C–H bonds of benzene noticably distorts its geometry, has a modest effect on the energies of the π MOs, and leaves the odd electron localized at the radical center.

As we go to higher members of the series, differences in geometry between the radicals and the parent arenes remain virtually the same.[22c] The energy of the SOMO is also not affected by ring expansion as shown in Table III.[23] Similar to the benzene–phenyl system, the energies of the various π MOs of aryl radicals are slightly stabilized relative to those of the parent arenes. Taking the pentacene–pentacenyl pair as an example (Table IV), the largest energy decrease was found to be 0.11 eV for the P1 MO. These small energy shifts do not really cause stabilization of the radical since they are compensated by destabilizing energy shifts (strain) in the σ MOs.[22]

The above ideas suggest that, even for an aryl radical derived from a long linear acene, where the σ and π states are expected to be the closest, the ground state is a σ state, and the doublet π state is considerably higher in energy. This can be seen simply by noting that the energy of the highest occupied π MO in a linear acene radical will occur at an energy near that for the parent infinite arene (specifically, at the energy of a 2p carbon orbital[19,24]) and that the energy of the SOMO σ orbital, since it depends little on the aromatic structure, is similar to the orbital in phenyl, which falls at a significantly higher energy.

Earlier INDO calculations[11] suggested that, upon ring expansion, the ground state of aryl radicals might change from σ to a π. Our own calculations show that this was an artifact caused by the lack of geometry optimization. If one arbitrarily fixes the geometry of the radical as that of the parent arene, these "single-point" calculations predict high-energy π ground states. When relaxation is fully allowed and one begins with geometries similar to that of phenyl, a lower energy σ state is approached.

Aryl–H Bond Strengths. Having shown that ground-state aryl radicals are σ radicals, we now examine the dependence of Ar–H bond strengths on aryl structure.

First, we compare calculated MNDO enthalpies of formation of arenes and phenyl radicals with the available experimental values (Table V).[25] The agreement between experimental and calculated heats of formation for the arenes is fair and comparable to other semiempirical methods.[26] The predicted heat of formation of phenyl radical is especially good, giving us added confidence that the computed differences in aryl–H bond strengths for different arenes will be reliable.

Second, we compare differences in MNDO bond strengths with differences in estimated arylation reaction thermodynamics derived from the present experimental work (Table VI). The agreement is good. It supports the simple assumption that differences in observed abstraction/arylation rates are primarily a result of different thermodynamic stabilities of the aryl radical reactant.

These findings are also consistent with the toluene carrier work of Ladaki and Szwarc.[27] They determined rates for homolysis of a series of monobromo aromatic compounds. Assuming the same *A* factor for all reactions, we can derive differences in C–Br bond strengths. These are compared with differences in corresponding MNDO C–H bond strengths in Table VI. Considering the small differences involved and uncertainties concerning strain in the aryl bromides, the agreement with both experimental and MNDO results is reasonable.

Finally, we attempt to generalize these findings. The results shown in Table VI suggest that aryl–H bonds can be roughly organized into three classes.[20] The first bonds are adjacent to two secondary, benzene-like carbon atoms and have a bond strength equal to that in benzene. Examples are the 2-naphthalenyl and 2-anthracenyl radicals. The second bonds are adjacent to one secondary and one tertiary "fused-ring" carbon and their bond strengths are weaker by 1–2 kcal/mol. Examples are the 1-naphthalenyl and 1-anthracenyl radicals. The third bonds are adjacent to two tertiary aromatic carbon atoms and have C–H bond strengths about 3–4 kcal/mol weaker than benzene. The 9-anthracenyl radical is an example. Since the infinite acene molecule has all its C–H bonds adjacent to two tertiary carbon atoms, all the C–H bonds in the limit of an infinite linear polyacene have comparable strengths, which are only 4–5 kcal/mol weaker than benzene.

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(23) (a) As pointed out by Clark,[15] the use of Koopman's theorem in connection to MNDO results for half-filled MOs is not correct. That is, equating the energy of the SOMOs of aryl radicals to their corresponding Koopman's ionization potentials is not valid. This is reflected when we compare the SOMO energy of phenyl, −4.86 eV, with its experimental ionization energy, 8.10 eV.[23b] Here, we are assuming that the error in the energy of the various SOMOs is constant for this homologous series. (b) Sergeev, Y. L.; Akipyan, M. E.; Vilesov, F. I. *Opt. Spectrosc.* (*Engl. Transl.*) **1971**, *30*, 121.

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J. Am. Chem. Soc. **1989**, *111*, 1423–1429

Summary

Experimental studies show that relative abstraction/arylation rates of polycyclic aromatic aryl radicals with toluene depend significantly on the structure of the aryl radical. Under the present conditions, the 9-anthracenyl radical, for instance, is about 15 times less likely to arylate toluene than is the phenyl radical. Relative rates of arylation at the different positions in toluene and naphthalene, on the other hand, are the same for all aryl radicals studied.

This behavior is interpreted to be a direct consequence of the reversibility for the addition of aryl radicals and the resulting sensitivity to differences in arylation thermodynamics. Theoretical analysis suggests that the thermodynamic differences arise primarily from inherent differences in stabilities of the aryl radicals as measured by differences in arene C–H bond strengths. It also indicates that, on the basis of bond strengths, three types of aryl radicals can be distinguished, typified by phenyl, 1-naphthalenyl, and 9-anthracenyl radicals. The size of the aromatic network has little if any effect on bond strengths. Instead, effects can be interpreted as a consequence of the local σ-bonding environment.

Acknowledgment. This work was supported by a grant from the Gas Research Institute.

Registry No. Toluene, 108-88-3; phenyl, 2396-01-2; 1-naphthalenyl, 2510-51-2; 2-naphthalenyl, 10237-50-0; 9-anthracenyl, 27735-77-9; hydrogen, 1333-74-0; naphthalene, 91-20-3; 9-phenanthrenyl, 20199-82-0; 9-tetracenyl, 61062-92-8; 1-pyrenyl, 27735-78-0; 2-pyrenyl, 61062-84-8; 3-pyrenyl, 27735-78-0; 9-pentacenyl, 118017-21-3; benzene, 71-43-2; anthracene, 120-12-7; phenanthrene, 85-01-8; naphthacene, 92-24-0; pyrene, 129-00-0; pentacene, 135-48-8.

The Thermal Decomposition of Hydroxy- and Methoxy-Substituted Anisoles

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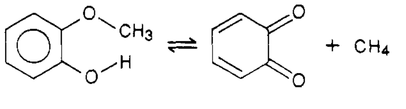
Received February 11, 1988

Abstract: Rates of decomposition of anisole and the three isomeric hydroxyanisoles and methoxyanisoles along with phenetole (ethoxybenzene) and *o*-hydroxyphenetole were determined in a very low pressure pyrolysis apparatus. In all reactions, the predominant process was O–methyl bond homolysis. Therefore, relative rates provide a quantitative measure of the effects of hydroxy and methoxy substituents on bond strengths in anisoles. A large bond-weakening effect was observed for the *o*-hydroxy group (7 kcal mol^{-1}), accounting for the exceptional lability of guaiacol observed in the condensed-phase studies of both Vuori and Virk. The *p*-hydroxy group weakened the anisole O–methyl bond by 2.5 kcal mol^{-1} and meta substitution had little effect. Both *o*- and *p*-methoxy groups weakened the O–methyl bond by 4 kcal mol^{-1} and *m*-methoxy substitution weakened this bond by 1 kcal mol^{-1}. Rates of all the reactions, when extrapolated to lower temperatures, were similar to rates of condensed-phase thermolysis reactions, indicating that homolysis is a key step in the liquid phase reactions. Other findings and conclusions are as follows: (1) Measured substituent effects do not correlate well with published rates of H abstraction from substituted phenols. (2) Bond breaking in anisoles occurs in a direct manner, without initial migration of the methyl group to the ring. (3) The generally observed higher reactivity of *o*-quinones than *p*-quinones may be due, in large part, to the special stabilization of the *o*-hydroxyphenoxy radical. (4) Theoretical (AM1) calculations yield the correct magnitude of the measured bond-weakening effects, but they do not reproduce important trends.

I. Introduction

Thermal decomposition reactions of substituted anisoles are of considerable current interest for two quite different reasons. First, since these structures are thermally labile constituents of lignin, their decomposition reactions serve as models for the pyrolysis of biomass and coal.[1-7] Second, homolysis rates of these molecules yield thermodynamic effects of substituents on bond strengths. Related substituent effects influence the effectiveness of phenolic antioxidants such as vitamin E[8] and BHT.[9]

Liquid-phase thermolysis studies by Vuori,[1] Bredenberg,[2-4] Schlosberg,[5], Virk,[6] and their co-workers of the decomposition of methoxy- and hydroxy-substituted anisoles and related compounds show that rates depend strongly on the position of substitution and that guaiacol (*o*-hydroxyanisole) is exceptionally labile. Sizable substituent effects were also found for *o*- and *p*-methoxyanisoles, although the reactivities of these were comparable. On the basis of the exceptionally rapid rate of decomposition of guaiacol, Klein and Virk[6] proposed the occurrence of a facile concerted reaction (reaction 1) in which methane and



(1)

o-quinone are formed directly, without the intermediacy of free radicals. However, more recently Vuori,[1] on the basis of measured relative spin concentrations in the pyrolyzed products, concluded that the concerted path made only a minor contribution. The nature of these initial products is of some significance to biomass and coal chemistry, since an inert species (methane) is generated in one case and a reactive intermediate (methyl radical) is formed in the other.

Most of the available data on the thermodynamics of phenoxy radicals comes from the work of Mahoney and co-workers.[10,11] Their work shows that substituents can have quite large effects. Further, for the series of molecules studied, they reported a strong correlation between rates of hydrogen abstraction from substituted phenols and phenolic O–H bond strengths. Partly on the basis

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