in this study could not be reliably identified as a product of reaction 4.

Conclusions

To our knowledge, these are the first thermal energy rate constants reported for the reactions of OH⁺ with CS₂, SO₂, NO₂, and NH_3 ; H_2O^+ with SO₂, N₂O, and CO₂; and H_3O^+ with CS₂, SO₂, and N₂O. Proton-transfer, charge-transfer, association, and atom abstraction reaction channels have been observed in this study. Association processes are observed for the reactions of H_2O^+ with N_2O and CO_2 and H_3O^+ with SO_2 and N_2O . The reaction of H_2O^+ with N_2O is of particular interest due to the identification of a second-order process in addition to the asso-

(39) Lias, S. G.; Liebman, J. F.; Levin, R. D. J. Phys. Chem. Ref. Data 1984, 13, 695

ciation. The proton-transfer and charge-transfer processes are competitive in many of the reactions involving OH^+ and H_2O^+ , although branching ratios were not obtained. The majority of rate coefficients for reactions involving a proton transfer are large and comparable to the calculated collision rate coefficients.

The rate constants determined for the charge-transfer reactions involving OH^+ and H_2O^+ in this study are also large. The Franck-Condon factors are interpreted from the PES of the neutral reactants and reveal that a number of the reactions do not possess Franck-Condon factors which are large in magnitude even though the reaction rates are fast. This agrees well with earlier results,14,25-29 further verifying that Franck-Condon considerations do not properly predict the magnitude of rate constants for thermal energy charge-transfer reactions.

Acknowledgment. Support by the National Science Foundation, Grant No. ATM-82-04010, is gratefully acknowledged. We thank Xiao-lin Yang for his assistance in performing the experiments and Dr. E. E. Ferguson for helpful comments on the paper.

Registry No. H₃O⁺, 13968-08-6; H₂O⁺, 56583-62-1; OH⁺, 12259-29-9; CS₂, 75-15-0; H₂S, 7783-06-4; SO₂, 7446-09-5; NO, 10102-43-9; NO2, 10102-44-0; N2O, 10024-97-2; N2, 7727-37-9; O2, 7782-44-7; CH4, 74-82-8; CO₂, 124-38-9; CO, 630-08-0; NH₃, 7664-41-7; H₂, 1333-74-0.

Gas-Phase Reactions of Phenyl Radicals with Aromatic Molecules

Askar Fahr and S. E. Stein*

Chemical Kinetics Division, National Bureau of Standards, Gaithersburg, Maryland 20899 (Received: November 18, 1987)

Relative rates of reactions of phenyl radicals with a series of aromatic and polycyclic aromatic compounds are reported. Most studies were done in static reactors at 450 °C using diphenyl diketone (benzil) as the phenyl radical source. Reactions with the following molecules are reported: benzene, toluene, p-xylene, 1,3,5-trimethylbenzene, phenol, bromobenzene, naphthalene, biphenyl, anthracene, 9-methylanthracene, and triphenylene. For reactions with substituted benzenes, H abstraction is the dominant reaction. Relative rates of phenylation at different sites do not closely follow established trends for rates of radical attack. It is proposed that these deviations are primarily due to a dependence of the degree of reversibility on the specific site of phenylation. These studies also show that the rates of phenyl and H-atom migration around the ring in adduct radicals are slow relative to dissociation. Also, by use of these results to link literature rate data from high and low temperatures, a rate expression for H abstraction from p-xylene by phenyl of $10^{9.6} \exp\{-4.4 \text{ kcal}/RT\}$ M⁻¹ s⁻¹ is derived.

Introduction

A considerable body of kinetic data exists for reactions of phenyl radicals in liquids in the range 25-150 °C.¹⁻³ These highly reactive radicals readily abstract H atoms and add to unsaturated bonds. Direct absolute rate measurements of their reactions with aromatic molecules show rate constants in the range 10⁶-10⁷ M⁻¹ s⁻¹ near room temperature.⁴

Although phenyl radicals are important intermediates in pyrolysis chemistry, rather few rate data are available at higher temperatures or in the gas phase. Two gas-phase studies of photochemically generated phenyl radicals were reported in 1962.5.6 These studies reported H-abstraction rates relative to phenyl recombination at temperatures near 350 °C. Both studies

Reversibility can significantly slow phenylation rates at elevated temperatures. Louw and Rothiuzen⁷ proposed that an observed low rate of toluene phenylation found by other workers in hightemperature gases was due to reversibility. In their own experiments they found that ortho phenylation of both chlorobenzene and cyanobenzene is less favored at high temperatures (400-500 °C) than at low temperatures (100 °C). This was also interpreted as a consequence of reversibility, ortho phenylation being more reversible than meta or para phenylation. On the basis of their measured temperature dependence of products in liquid-phase reactions, Henriquez et al.⁸ suggested that addition is reversible above 100 °C. We have recently measured rates of phenylation of ethyne, ethene, and benzene relative to phenyl recombination in a low-pressure flow reactor at 550-950 °C.9 Observed deu-

⁽⁴⁰⁾ CRC Handbook of Chemistry and Physics, 62nd ed.; CRC: Boca Raton, FL, 1982; p E-60.

⁽⁴¹⁾ McDaniel, E. W.; Mason, E. A. The Mobility and Diffusion of Ions *in Gases*; Wiley: New York, 1973; pp 344–346. (42) Dotan, I.; Lindinger, W.; Rowe, B.; Fahey, D. W.; Fehsenfeld, F. C.;

Albritton, D. L. Chem. Phys. Lett. 1980, 72, 67.

⁽⁴³⁾ Durup-Ferguson, M.; Böhringer, H.; Fahey, D. W.; Ferguson, E. E. J. Chem. Phys. 1983, 79, 265.

⁽¹⁾ See, for example: Free Radicals; Kochi, J., Ed.; Wiley: New York, 1973; Chapters 2, 67, 16.
(2) Denisov, E. T. Liquid Phase Reaction Rate Constants; Plenum: New

⁽²⁾ Domot, D. A. Lynn, C. M. J. Am. Chem. Soc. 1963, 85, 3754.
(3) Bridger, R. F.; Russell, G. A. J. Am. Chem. Soc. 1963, 85, 3754.
(4) Sciano, J. C.; Stewart, L. C. J. Am. Chem. Soc. 1983, 105, 3609.
(4) Sciano, J. C.; Stewart, L. C. J. Am. Chem. Soc. 1962, 462.

Duncan, F. J.; Trotman-Dickinson, A. F. J. Chem. Soc. 1962, 462. (6) Fielding, W.; Pritchard, H. O. J. Phys. Chem. 1962, 66, 821.

encountered chemical complexities, and for the only reactant molecule common to the two studies (CH_4) , rate constants differed by a factor of 4. No reactions with aromatic molecules were studied.

⁽⁷⁾ Louw, R.; Rothuizen, J. W. *Tetradron Lett.* 1967, 39, 3807.
(8) Henriquez, R.; Morgan, A. R.; Mulholland, P.; Nonhebel, D. C.;

Smith, G. G. J. Chem. Soc. 1974, 987.

Fahr and Stein

TABLE I: Relative Molar Concentrations^a of Reaction Products of $(PhCO)_2 - /p$ -Xylene Mixtures (T = 450 °C, t = 30 min)

	10-										
(PhCO) ₂ -/ <i>p</i> -xylene	mix. vol/ cell vol	PhH	PhCH ₃	PhPh	<i>p</i> - PhPhCH ₃	<i>m</i> -Ph- <i>p</i> -xylene	<i>p</i> - CH₃PhCH₂Ph	PhCOPh	(CH ₃ PhCH ₂) ₂ -	PhCOCH ₂ - PhCH ₃	mass balance ^b
0.01	10	0.367	с	с	0.011	0.027	0.008	0.024	0.212	0.028	0.96
0.01	1.7	0.420	с	с	0.012	0.031	0.003	0.017	0.264	0.019	0.87
0.03	5	0.590	0.016	0.007	0.015	0.042	0.014	0.016	0.319	0.038	1.01
0.03	5	0.576	0.022	0.003	0.013	0.033	0.013	0.018	0.324	0.040	0.96
0.03	5	0.684	0.021	0.010	0.019	0.046	0.021	0.019	0.334	0.049	1.12
0.03	10	0.560	0.023	0.011	0.016	0.042	0.020	0.023	0.311	0.048	0.99
0.03	20	0.621	0.041	0.016	0.019	0.046	0.023	0.020	0.307	0.044	1.12
0.03	20	0.660	0.060	0.004	0.019	0.050	0.029	0.017	0.361	0.061	1.01
0.10	5	0.517	0.016	0.015	0.015	0.037	0.018	0.015	0.258	0.037	1.10
0.10	5	0.514	0.011	0.012	0.014	0.038	0.021	0.015	0.247	0.400	1.14
0.10	10	0.487	0.030	0.018	0.015	0.037	0.023	0.014	0.264	0.059	1.02
0.10	1.3	0.347	0.014	0.002	0.010	0.027	0.013	0.012	0.220	0.065	0.87

^a Molar concentrations relative to the concentration of the remaining $(PhCO)_2$ -. ^bMass balance = $([PhH] + [PhPhCH_3] + [PhPh(CH_3)_2])/(2[(CH_3PhCH_2)_2-])$. ^cUndetectable quantities.

terium kinetic isotope effects and thermochemical calculations both indicated that addition is reversible. Unfortunately, none of these studies provide a reliable quantitative measure of the degree of reversibility.

In the present work, we report relative rate measurements of gas-phase reactions of phenyl radicals with a series of aromatic compounds. This provides the first gas-phase data on relative rates of abstraction and phenylation. In accord with the findings of Louw and Rothiuzen,⁷ when compared to results obtained at lower temperatures these results suggest that both relative and absolute rates of phenylation are affected by reversibility. Also, together with literature rate constants,^{4,9} these rate data enable us to derive an Arrhenius expression for H transfer from *p*-xylene over the range 25-450 °C and thereby obtain absolute rate values for phenylation reactions over a wide range of temperature.

Experimental Section

All reactions were done in evacuated, sealed Pyrex tubes (typically, 3-mm i.d. \times 50-mm length). Reaction mixtures were transferred to reaction tubes by syringe, except for reactions involving compounds of low solubility, which were added directly to the tubes. Tubes were heated in a fluidized bath maintained at a temperature held constant to ± 1 °C. Most reactions were done at 450 °C, and mole fractions of initiators were 0.01–0.1. Under these conditions, reaction extents of the initiator (benzil) varied from 20% to 60% as reaction times were varied from 15 min to 1 h. Typically, liquid sample volumes were 2–5 μ L, resulting in pressures during the reaction of 2–5 atm.

Reaction mixtures contained a thermal radical initiator (in most cases benzil, PhCOCOPh, was used for this purpose although benzaldehyde/1,2-diphenylethane mixtures were used in a few cases), an H-atom donor (most often p-xylene), and in many cases a phenylation target compound. Quantitative analysis was done by glass-capillary gas chromatography with flame ionization detection. Thermolysis mixtures were diluted with n-propylbenzene prior to analysis. Products were identified by co-injection (when authentic samples were available), GC/MS, and structure/retention time relations (i.e., retention times for phenyl substitution increase in the order ortho \ll meta < para and 1-phenyl < 2-phenyl¹⁰). Phenylation products identified solely by their mass spectra and relative retention times were 1,4-dimethylbiphenyl, 3,5-dimethylbiphenyl, 2,4,6-trimethylbiphenyl, 1- and 2-phenylanthracene, 1- and 2-phenyltriphenylene, and 10-methyl-9-phenylanthracene.

Results and Overall Mechanism

Reactions of phenyl radicals with *p*-xylene were examined in the greatest detail. Selected results are given in Table I. No systematic variations of relative product yields were found as a function of reaction time, total pressure, or mole fraction of radical initiator (benzil). The general mechanism for reactions of phenyl radicals is illustrated in eq 1–6 for reaction with p-xylene. In this

 $PhCOCOPh \rightarrow 2PhCO \rightarrow 2Ph + 2CO$ (1)

$$Ph \cdot + H_3C(C_6H_4)CH_3 \rightarrow Ph[H_3C(C_6H_3)CH_3] + H \cdot (3)$$

$$Ph \cdot + H_3C(C_6H_4)CH_3 \rightarrow Ph(C_6H_4)CH_3 + CH_3 \cdot (4)$$

$$CH_3 \cdot$$
) + $H_3C(C_6H_4)CH_3 \rightarrow$

$$H_3C(C_6H_4)CH_2 + H_2(CH_4)$$
 (5)

$$2H_3C(C_6H_4)CH_2 \rightarrow [H_3C(C_6H_4)CH_2-]_2$$
(6)

case, *p*-xylene served as both the H donor and the phenylation target molecule. Since each of the reaction channels for phenyl radical + p-xylene leads to a unique, stable product, relative product yields were a direct measure of relative rate constants. According to this mechanism, the sum of moles of benzene and the phenylation products should be twice the number of moles of 4,4'-dimethylbibenzyl. As shown in Table I, this relation holds reasonably well.

Three side products (I-III) possibly resulting from the reaction



of p-xylyl radicals with benzil, were observed. The formation of I may result from simple displacement of a benzoyl group in benzil by p-xylyl radicals. In support of this idea, we found that the ratio of I to the p-xylyl recombination product increased approximately with the square root of benzil concentration.

Rate estimates indicate that II is not formed by the recombination of phenyl and p-xylyl radicals, even at the highest concentrations of benzil. Moreover, the kinetics of formation of II are not consistent with this process. However, we cannot find a convincing explanation for the formation of either II or III.

Only very small amounts of toluene were formed ([toluene]/ [benzene] ≈ 0.05), indicating that displacement reactions involving H atoms were unimportant. We therefore assume that none of the benzene observed was formed by H-atom attack of benzil.

In all reactions, biphenyl was detected as a minor product. Both the kinetics of its formation and rate estimates showed that it was not formed by recombination of phenyl radicals.

From total yields of products from reactions of phenyl radicals we derive a rate constant for unimolecular dissociation of benzil of 2.0×10^{-4} s⁻¹ at 450 °C. This is nearly the same the extrapolated value of Jacquiss and Szwarc (1.7×10^{-4} s⁻¹).¹¹

⁽⁹⁾ Fahr, A.; Mallard, W. G.; Stein, S. E. Proc. 21st Int. Symp. Combust., Combust. Inst., Pittsburgh, PA, 1987.
(10) Lee, M. L; Novotny, M. V.; Bartle, K. D. Analytical Chemistry of

⁽¹⁰⁾ Lee, M. L; Novotny, M. V.; Bartle, K. D. Analytical Chemistry of Polycyclic Aromatic Compounds, Academic: New York, 1981.

TABLE II: Reactions of Phenyl Radicals with Substituted Aromatic Compounds

•						
reactant	reaction ^a	$k/k_{\text{H-disp}}(p\text{-xylene})$				
*	H-abs H₂-disp H₃-disp H₄-disp	7.5 \pm 0.7, (8.1) ^b \pm 0.5 0.40 \pm 0.03, (0.41) ^b \pm 0.03 0.75 \pm 0.03, (0.73) ^b \pm 0.03 0.40 \pm 0.01, (0.42) ^b \pm 0.08				
СН3-СН3	H-abs H-disp CH3-disp	$14.2 \pm 1.1 (1.0) 0.38 \pm 0.02$				
CH3 CH3 CH3	H-abs H-disp CH3-disp	$23.7 \pm 1.6 0.77 \pm 0.17 0.78 \pm 0.14$				
	H-abs H ₁ -disp H ₂ + H ₃ -disp H ₄ -disp H ₉ -disp CH ₃ -disp	$11.6 \pm 1.6 6.6 \pm 0.2 10.1 \pm 0.5 7.9 \pm 0.6 25.4 \pm 4.3 32.6 \pm 2.5$				
3 2 • ОН	H-abs H ₂ -disp H ₃ -disp H ₄ -disp OH-disp	$\begin{array}{l} 17.5 \pm 0.7 \\ 1.38 \pm 0.21 \\ 0.86 \pm 0.12 \\ 0.56 \pm 0.04 \\ 0.18 \pm 0.04 \end{array}$				
4 Br	Br-disp H₂-disp H₃-disp H₄-disp	$\begin{array}{l} 0.36 \pm 0.02 \\ 0.48 \pm 0.02 \\ 1.21 \pm 0.03 \\ 0.62 \pm 0.03 \end{array}$				

^aH-abs = H-atom abstraction; H_n -disp = H-atom displacement (phenylation) at position *n*; CH_3 -disp = methyl displacement; OH-disp = hydroxyl displacement; Br-disp = bromine displacement. ^bUsing benzaldehyde as the phenyl radical source. Note: Error limits are standard deviations based, typically, on four separate runs.

To confirm that results were independent of initiator, we used a mixture of benzaldehyde and 1,2-diphenylethane as the phenyl radical source for reactions with toluene. In this system, phenyl radicals are formed by the following reaction sequence:

 $PhCH_2CH_2Ph \rightarrow 2PhCH_2$

$$PhCHO + PhCH_2 \rightarrow PhCO + PhCH_3$$

 $PhCO \rightarrow Ph + CO$

Results of these studies were the same as those obtained in benzil-containing systems (Table II). In all other studies, benzil was the initiator.

Greater than 95% of the benzene formed in reactions with toluene- d_8 was singly deuteriated, indicating that H abstraction from impurities did not contribute significantly to benzene formation. Experiments with toluene-*methyl*- d_3 showed that >90% of H abstraction from toluene occurred at the methyl position rather than a ring position (a benzene impurity in toluene-*methyl*- d_3 prevented a more precise determination of this ratio).

Table II summarizes results of studies of phenyl radicals with the six substituted aromatic compounds examined in this work: p-xylene, toluene, 1,3,5-trimethylbenzene, 9-methylanthracene, phenol, and bromobenzene. For each of the last five compounds, studies were also done in the presence of p-xylene. Relative phenylation/abstraction rates were determined from the relative amounts of phenylation/benzene products. Rates are given relative to the rate of aromatic H-atom displacement in p-xylene.

Results of experiments involving mixtures of *p*-xylene and selected (poly)aromatic molecules are given in Table III. Rates of phenylation at each distinguishable position are given relative to rates of H-atom displacement in *p*-xylene. Also shown are

 TABLE III: Phenylation of Unsubstituted (Polycyclic) Aromatic Compounds

reactant	position	$k/k_{\rm H-disp}(p-xylene)$
\bigcirc		1.46 ± 0.11
C_6D_6		0.98 ± 0.07
	1 2	2.81 ± 0.26 3.75 ± 0.40
$C_{10}D_{8}$	1 2	1.47 ± 0.08 1.86 ± 0.26
	1 2 9	8.8 ± 1.1 9.6 ± 1.6 27.6 ± 3.2
C ₁₄ D ₁₀	1 2 9	4.63 ± 0.32 5.10 ± 0.41 17.8 ± 1.2
٠ • •	2 3 4	0.67 ± 0.11 2.47 ± 0.37 1.57 ± 0.21
\bigcirc	1 2	1.2 ± 0.4 8.5 ± 2.0

theoretical (HMO) electron localization energies (expressed as H-atom affinities).

Discussion

Phenylation. Phenylation takes place through a two-step process. The first is phenyl addition to the ring (reaction 7), and the second is displacement of the substituent (or H atom) at the site of attack (reaction 8).

$$Ph \bullet + R - C = C \xrightarrow{k_7} Ph - C - C \bullet (7)$$

$$Ph - C - C \cdot \xrightarrow{k_8} Ph - C = C + R \cdot$$
(8)

Rate estimates show that under the present conditions phenyl addition to a site of methyl substitution invariably leads to displacement (i.e., $k_{\text{phenylation}} = k_7$). The adduct formed by addition to an H-substituted site will, on the other hand, often redissociate. Thermochemical estimates suggest that k_{-7}/k_8 falls in the range 1–10 for phenylation of benzene.⁹

Assuming reversibility $(k_{-7}/k_8 > 1)$, the rate of phenylation may be approximately expressed as the product of the equilibrium constant for phenylation and the rate of ipso (at the site of substitution) H-atom attack of the phenylated product (expression 9). This expression, in effect, separates thermodynamic and

$$k_{\text{phenylation}} = K_{\text{eo}}(\text{Ph} + \text{Ar} - \text{H} \rightleftharpoons \text{Ph} - \text{Ar} + \text{H})k_{-8} \quad (9)$$

kinetic contributions to the observed phenylation rate.

Phenyl + *p-Xylene*. Relative to H-atom abstraction, rates for H-atom and methyl displacement by phenyl radicals were 0.07 and 0.03, respectively. These low values are consistent with previous qualitative findings.⁶ Since the former reaction is reversible and the latter is not, the preference for addition to the unsubstituted site is actually greater than 0.07/0.03. On the other hand, since ipso addition is irreversible, the 0.03 value is the actual relative rate for ipso addition and H abstraction.

Phenyl + Toluene. Reactions of phenyl radicals were studied in both toluene and toluene/p-xylene mixtures. As might be expected, relative rates for abstraction and ortho-H displacement from toluene were nearly the same as for p-xylene. Rates of methyl displacement could not be reliably determined since small amounts of biphenyl were also formed as a side product in the reaction of benzil. Rates of phenylation per position at the meta and para positions were nearly equal, indicating that the methyl

⁽¹¹⁾ Jacquiss, Ph.D. Thesis, Manchester, 1953, as cited in: O'Neal, H. E.; Benson, S. W. *Kinetis Data on Gas Phase Unimolecular Reactions*; NSRDS-NBS 21; U.S. Government Printing Office: Washington, DC, 1970; p 421.

					lit.		H-atom ^e	
reactant	position of attack	$\frac{\text{present work}}{k^a/k(\text{benzene})} \% \text{ isome}$		$10^{-6}k$, M ⁻¹ s ⁻¹	k/k(benzene)	% isomer	affinity, kcal	
$\langle \bigcirc \rangle$		(1)		0.45 ^b	(1)		(22)	
4	2 3 4	0.27 0.51 0.27	$ \left.\begin{array}{c} 26\\ 48\\ 26 \end{array}\right\} $	1.7 ^b		59 ^d 17 ^d 24 ^d		
	1 2	1.93 2.57	43 57		13.7° 2.3°	85 ^d 15 ^d	32.4 24.4	
	1 2 9	6.0 6.6 18.9	19 21 60		31.8° 9.3° 227°	12° 4° 84°	35.4 27.0 44.9	
<u>م</u>	2 3 4	0.46 1.70 1.07	14 53 33			38 ^d 18 ^d 44 ^d	27.0 21.6 25.9	
	1 2	0.82 5.82	12 88				28.9 24.5	

TABLE IV: Comparison of Present and Literature Phenylation Rate Data

 ${}^{a}k$ (benzene) = 1.6 × 10⁷ M⁻¹ s⁻¹ with data from ref 9 extrapolated to temperatures of the present work with an A factor of 10⁹ M⁻¹ s⁻¹. ${}^{b}Reference 4, T = 25$ °C. ${}^{c}Reference 17, T = 30$ °C. ${}^{d}Reference 15, T = 80$ °C. ${}^{e}Based on Hückel MO calculations assuming an H-atom affinity for benzene of 22 kcal/mol.¹³$

TABLE V: Relative Rates (per Position) of Toluene and Benzene Phenylation from Different Reaction Mixtures

mixture	<i>m</i> -toluene/ benzene	p-toluene/ benzene
toluene/benzene	1.33 ± 0.15	1.46 ± 0.15
(diphenylmethane/benzene)	1.54 ± 0.16	1.70 ± 0.17
toluene/p-xylene (p-xylene/benzene)	1.53 ± 0.14	1.65 ± 0.13

group had little net inductive effect. Ortho phenylation was only half as fast as meta phenylation. This is in sharp contrast to the results of liquid-phase phenylation studies of Augood et al.,¹² where at 25 °C ortho phenylation was 3.5 times faster than meta phenylation (Table IV). It is therefore likely that the relatively low rate of ortho phenylation in the present high-temperature experiments is a result of an increased degree of reversibility caused by steric interference in the phenylation product (ortho-methyl biphenyl). Generally similar trends in the change of isomer distribution in going from low-temperature liquids to high-temperature gases was observed by Louw and Rothuizen⁷ in their studies of the phenylation of chlorobenzene and cyanobenzene.

Phenyl + 1,3,5-*Trimethylbenzene*. Relative rates of H abstraction, H-atom displacement, and methyl displacement per site were similar to those of *p*-xylene. The presence of a second methyl group adjacent to the reaction site had little net effect on the H-displacement rate.

Phenyl + *Benzene*. On a per site basis, phenylation of benzene occurred at 65% of the rate of phenylation at the meta or para positions in toluene. Although we had expected these rates to be identical, we believe this difference to be outside the range of experimental error. Similar values for this ratio were obtained in three independent relative rate measurements (Table V).

Using eq 9 as a guide, we can suggest two possible reasons for this difference: (1) Phenylation of toluene is more favored thermodynamically than is phenylation of benzene. Specifically, this requires that the methyl group in toluene stabilizes both metaand para-phenylation products by 0.5 kcal/mol. (2) The methyl group lowers the intrinsic Gibbs activation energy for H loss (i.e., it increases the rate of the reverse H-addition process by ca. 40%). We cautiously favor explanation 1 because addition reactions of H atoms are not expected to be so selective at the temperatures of these experiments.

An additional factor to consider is the possible migration of a phenyl group in the radical adduct prior to dissociation. This conjecture was tested for migration to substituted positions (see below). Phenylation of benzene- h_6 was approximately 50% faster than benzene- d_6 . A similar effect was observed in previous flow experiments near 1000 K.⁹ We believe that these are primary isotope effects arising from different rates of H- and D-atom loss from the adduct, providing further evidence that addition is reversible.

Phenyl + Phenol. The net rate of H abstraction from phenol and *p*-xylene were comparable. Whereas ortho phenylation of toluene was one-half as fast as meta phenylation, in phenol ortho phenylation was actually 50% faster.

Phenyl + Biphenyl, Naphthalene, Anthracene, and Triphenylene (IV). Relative rates of phenylation at structurally



related positions (e.g., at 1-positions) in these molecules are roughly of the same order as their relative Hückel MO electron localization energies (see Table IV).¹³⁻¹⁶ Electron localization energies represent the loss of π -electron energy upon "localizing" a π electron. They correlate well with radical addition rates. But for reactions at different sites in the same molecule, this correlation does not hold. Contrary to differences in localization energy, phenylation at the 2-position is faster than 1-phenylation in naphthalene, anthracene, and triphenylene. Assuming reversibility for addition, this indicates that 2-phenylated products are more stable than 1-phenylated products (see eq 9). While we cannot

⁽¹³⁾ Stein, S. E.; Brown, R. L. J. Am. Chem. Soc. 1987, 109, 3721.
(14) Dickerman, S. C.; Feigenbaum, W. M.; Fryd, M.; Milstein, N.;
Vermont, G. B.; Zimmerman, I.; McOmie, J. F. W. J. Am. Chem. Soc. 1973, 95, 4624.

 ⁽¹⁵⁾ Streitwieser, A., Jr.; Lewis, A.; Schwager, A.; Fish, R. W.; Labana,
 S. J. Am. Chem. Soc. 1970, 92, 6529.

⁽¹⁶⁾ Dewar, M. J. S. The Molecular Orbital Theory of Organic Chemistry; McGraw-Hill: New York, 1976.

⁽¹²⁾ Augood, D. R.; Williams, G. H. Chem. Rev. 1957, 57, 123.

Gas-Phase Reactions of Phenyl Radicals

find external evidence for this, it is consistent with the higher degree of planarity in the 2-phenylated molecules (hence, greater resonance conjugation and lower barrier in internal rotation). The very low rate of phenylation of the 1-position in triphenylene is clearly a consequence of the instability of the highly hindered 1-phenylation product. The very high reactivity of the 9-position of anthracene apparently more than compensates for the extra crowding in the 9-phenylanthracene product. The finding that the phenylation rate per site at the meta position of biphenyl was about 2.5 times that in benzene was unexpected. It may indicate that phenylation of biphenyl at both the meta and para positions is ca. 1 kcal/mol more exothermic than phenylation of benzene.

Phenyl + 9-Methylanthracene. In accord with differences in reaction thermodynamics, H abstraction from the methyl group in 9-methylanthracene is faster than abstraction from the methyl group in toluene (the former abstraction is ca. 6 kcal/mol more exothermic than the latter¹⁷). This rate difference is, however, by only a factor of 4. This modest difference is not unexpected in view of the high exothermicity for both reactions.

Phenyl + Bromobenzene. We surmised that product distributions might be affected if the adducts formed by phenyl addition isomerized by a "neophyl" rearrangement:¹⁸



Phenylation studies of bromobenzene were carried out to test this idea. If migration were rapid, biphenyl would be the major product, since the relatively weak C-Br bond would immediately break once the phenyl had migrated to the brominated carbon atom. However, a distribution of isomers not drastically different from that for toluene was found, with the products biphenyl, o-bromobiphenyl, m-bromobiphenyl, and p-bromobiphenyl in the ratio 0.75:1.0:2.5:1.3. These studies imply that phenyl migration is not fast in the adduct radical.

These findings also show that H-atom migration around the ring is much slower than H dissociation, since rapid H-atom migration would have led to displacement of bromine just as illustrated above for phenyl migration. This implies that H-atom addition reactions to substituted aromatic molecules can only result in displacement if the addition is directly to the site of substitution. Absolute Rate Constants. An Arrhenius expression for H abstraction by phenyl radicals may be obtained by combining the present relative rate data with room-temperature data of Sciano and Stewart⁴ and phenylation rates obtained at 1000 K.⁹ We do this by first extrapolating the high-temperature value for the phenylation of benzene to the temperature of the current experiments (450 °C) with an assumed A factor of 10⁹ M⁻¹ s⁻¹. Using the finding that H abstraction from *p*-xylene is 10 times faster than phenylation of benzene, we obtain a rate constant for the abstraction reaction of $10^{7.7}$ M⁻¹ s⁻¹ at 450 °C. Assuming that the reaction of phenyl radical with *p*-xylene at room temperature occurs primarily by H abstraction, Sciano and Stewart's value for this reaction of $10^{6.5}$ M⁻¹ s⁻¹. These Arrhenius parameters would be higher if addition were a significant process in the low-temperature reaction.

Summary and Conclusions

Our analysis suggests that relative rates of H displacement by phenyl radicals at elevated temperatures depend on the degree of reversibility of addition. This leads to patterns of reactivity different from that of simple addition reactions. In these phenylation reactions, differences in overall reaction thermodynamics directly impact relative phenylation rates. In naphthalene and anthracene, for instance, the 2-position, normally the least reactive, is actually phenylated more rapidly than the 1-position. We suggest that the steric crowding in the phenylated product is the principal cause of this difference.

Even though H displacement is slowed by reversibility, it still is generally faster than methyl displacement, an irreversible process. However, benzylic H-abstraction reactions are usually even faster.

Our observations that meta phenylation of toluene is measurably faster than that of benzene (per site) and that meta phenylation of biphenyl is faster than that of toluene were unexpected. This my be as a result of small differences between the thermodynamics of phenylation of these molecules.

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

Registry No. I, 2430-99-1; II, 620-83-7; III, 119-61-9; IV, 217-59-4; (PhCO)₂, 134-81-6; PhH, 71-43-2; PhCH₃, 108-88-3; PhPh, 92-52-4; *p*-PhPhCH₃, 644-08-6; *m*-Ph-*p*-xylene, 7372-85-2; (CH₃PhCH₂)₂, 538-39-6; phenyl radical, 2396-01-2; *p*-xylene, 106-42-3; 1,3,5-trimethylbenzene, 108-67-8; phenol, 108-95-2; bromobenzene, 108-86-1; naphthalene, 91-20-3; anthracene, 120-12-7; 9-methylanthracene, 779-02-2.

⁽¹⁷⁾ Stein, S. E. In *Chemistry of Coal Conversion*; Schlosberg, R. H., Ed.; Plenum: New York, 1985; p 13.

⁽¹⁸⁾ See ref 1, Chapter 8.