(4:6 vol. %). The homogeneous reaction mixture was allowed to stand in a flask with a loosely held glass stopper without stirring; no difference in rates was observed between reactions with and without stirring. Aliquots were taken out at appropriate intervals of time, and the produced aldehyde was estimated by means of ultraviolet spectrophotometry after extracting with chloroform as reported previously.[3]

Materials. Substituted benzyl methyl ethers except the *p*-methoxy derivative were prepared by way of the side-chain bromination of corresponding toluenes, followed by treatment with sodium methoxide. *p*-Methoxybenzyl ether was synthesized by the bromination of *p*-methoxybenzyl alcohol[3] by the hydrogen bromide method,[19] followed by methanolysis with sodium methoxide. Benzyl alkyl ethers were obtained by the treatment of benzyl chloride with sodium alkoxide at the reflux temperature for 3–4 hr. The ethers were all purified by rectification under vacuum (Table VIII).

The other materials were the same with those described previously.[3]

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(19) R. B. Woodward, *J. Am. Chem.Soc.*, **62**, 1478 (1940).

Rates of Bromination of Polynuclear Aromatic Hydrocarbons[1]

Lili Altschuler[2] and Ernst Berliner[3]

Contribution from the Marion Edwards Park Laboratory of Bryn Mawr College, Bryn Mawr, Pennsylvania. 19010. *Received August 15, 1966*

Abstract: Rate constants for the bromination of several polynuclear aromatic hydrocarbons by molecular bromine were determined in aqueous acetic acid at 25°. Partial rate factors were obtained from the rates and the major reaction products. The partial rate factors, and some obtained previously, were correlated with MO reactivity parameters and with the rates of other electrophilic substitution reactions. Addition accompanies substitution in the bromination of phenanthrene and anthracene.

Although interest in the reactivities of polynuclear aromatic systems has increased as a result of the availability of various MO reactivity parameters with which the experimental reactivities can be compared, there are only very few reactions series in which these reactivities have been assessed in direct electrophilic substitution reactions. The studies that cover the largest number of compounds are those on nitration,[4] deuterio deprotonation,[5] the basicity toward hydrogen fluoride,[6] and, to a lesser extent, chlorination.[7] To these we now add bromination.

Results

Reactions were carried out in aqueous acetic acid. In acetic acid, as well as in other solvents of low dielectric constant, the kinetics of bromination is complicated by the intervention of terms which are of high order in bromine, and by the complexing of unreacted bromine with bromide ion which is formed as the reaction proceeds.[8] It is for this reason that investigations that did employ bromination for a comparison of relative rates have often relied on a comparison of time intervals required to reach a definite per cent of reaction, and rate constants were not determined. For instance, in an earlier study of bromination, Mason compared the times for 5 and 10% bromination of hydrocarbons in 80% acetic acid.[9] Under these conditions, the bromination of benzene, naphthalene, and biphenyl was approximately third order over-all, but the reaction of phenanthrene followed second-order kinetics. Its reactivity could therefore not be compared with that of the other compounds. It would seem, then, that the method of comparing reaction times is beset by hazards, particularly if the compounds differ widely in reactivity.

The reasons for the complexity of aromatic bromination are now well understood, and conditions have been worked out under which the high orders in bromine can be reduced and the reaction conducted under conditions such that the total order of reaction is two, first order in both hydrocarbon and stoichiometric bromine. This can be accomplished by increasing the water content, or, more importantly, by conducting the reaction in the presence of a large excess of bromide ion.[10] Under these conditions, much of the bromine is complexed to tribromide ion, which reduces the free bromine concentration to such small amounts that the high-order terms become negligible.[11] Also, since most of the bromine is present as tribromide ion, the small amount of bromide ion that is formed during reaction does not interfere with the second-order kinetics. It has previously been shown that under those conditions the relationship $k_{\text{obsd}} = k_2K/(K + \text{Br}^-)$ (eq 1) holds, where k_2 is the rate constant for bromination by free bromine and K the dissociation constant of the tribromide ion. Rate constants are determined at various bromide ion concentrations at a constant ionic strength, and the true rate constant, k_2, is obtained as the slope

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(1) Relative Reactivities of Polynuclear Aromatic Systems. IV.

(2) Taken from the Ph.D. thesis of L. Altschuler, Bryn Mawr College, May 1966.

(3) To whom inquiries should be addressed.

(4) M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956).

(5) G. Dallinga, A. A. V. Stuart, P. J. Smit, and E. L. Mackor, *Z. Elektrochem.*, **61**, 1019 (1957).

(6) E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 66, 186 (1958).

(7) M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 342 (1957); S. F. Mason, *ibid.*, 1233 (1959).

(8) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworth & Co., Ltd., London, 1959, Chapter 9; P. W. Robertson, P. B. D. de la Mare, and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943); P. B. D. de la Mare and P. W. Robertson, *ibid.*, 100 (1948); R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **78**, 3637 (1956).

(9) S. F. Mason, *J. Chem. Soc.*, 4329 (1958).

(10) E. Berliner and M. C. Beckett, *J. Am. Chem. Soc.*, **79**, 1425 (1957).

(11) U. P. Zimmerman and E. Berliner, *ibid.*, **84**, 3953 (1962).

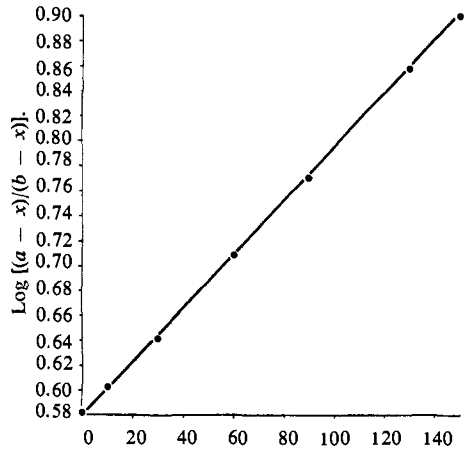

Figure 1. A second-order plot for the bromination of fluoranthene in 75% acetic acid at 25°. Fluoranthene 0.007443 *M*, Br_2 0.001949 *M*, Br^- 0.15 *M*.

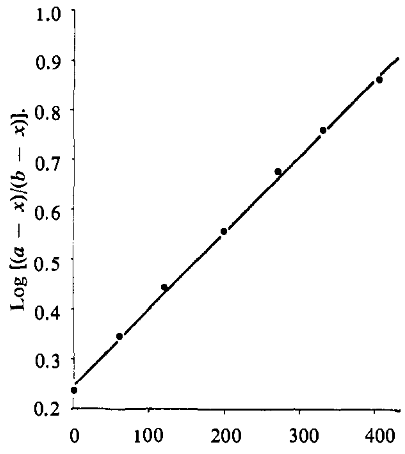

Figure 3. A second-order plot for the bromination of 1,2-benzanthracene in 90% acetic acid at 25°. 1,2-Benzanthracene 0.001613 *M*, Br_2 0.000897 *M*, Br^- 0.25 *M*.

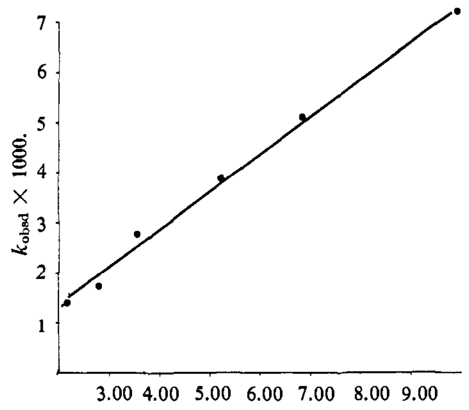

Figure 2. The dependence of the rate of bromination of phenanthrene on the bromide ion concentration in 75% acetic acid at 25°. Slope 0.0755 ± 0.0018, intercept −0.0001 ± 0.0001.

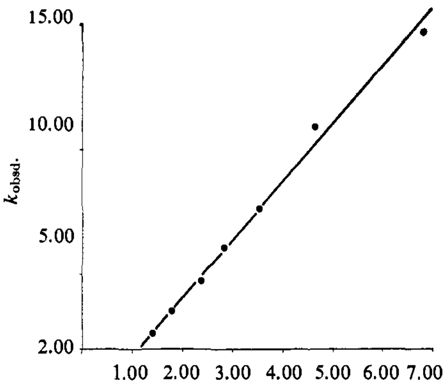

Figure 4. The dependence of the rate of bromination of pyrene on the bromide ion concentration in 90% acetic acid at 25°. Slope 233 ± 4, intercept −0.63 ± 0.15.

on plotting k_{obsd} against $K/(K + Br^-)$. This form of the rate equation has been shown to apply to bromination in 50,[10] 60,[12] and 75%[11] aqueous acetic acid, and establishes molecular bromine as the substituting agent in a reaction in which the attack of bromine on the aromatic compound is rate determining.

In this study, rates of bromination of the typical aromatic hydrocarbons phenanthrene, pyrene, 1,2-benzanthracene, chrysene, and anthracene were determined under the kinetic conditions outlined above. Fluoranthene, a typical nonalternant benzenoid hydrocarbon, was also investigated. Rates and product distribution had previously been determined for benzene,[13] biphenyl,[13] naphthalene,[14] and fluorene.[11] The rates of reaction of phenanthrene and fluoranthene were determined in 75% aqueous acetic acid (by volume, before mixing), those of the other compounds in 90% acetic acid. The determining factor in choosing these conditions is the very low solubility of most hydrocarbons in these solvents, and to a lesser extent their reactivity, which decreases in the less aqueous solvent.

The reactions of fluoranthene and phenanthrene in 75% acetic acid were second order, as had previously been demonstrated for fluorene.[11] Runs were conducted at different bromide ion concentrations at a constant ionic strength at 25°. Rate constants (k_{obsd}) were determined graphically from plots of the integrated rate equation. A typical plot for bromination of fluoranthene is shown in Figure 1. The true rate constants, k_2, were then obtained from a least-square plot according to eq 1. This is shown for the bromination of phenanthrene in Figure 2. Individual rate constants are reported in Table I.

The bromination of the other hydrocarbons was conducted in 90% aqueous acetic acid. In the presence of an excess of bromide ion, the reaction in the less aqueous solvent is also second order over-all. A typical second-order plot is shown for the bromination of 1,2-benzanthracene in Figure 3. Because the exact kinetic dependence of the rate on initial concentrations of reactants had not been previously demonstrated for this solvent, the bromination of pyrene was studied in greater detail by varying the concentration of bromine and the hydrocarbon. The data in Table I show that the reaction is first order in pyrene and in bromine, and that a twofold variation of hydrocarbon concentration and an eightfold variation of bro-

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(12) E. Berliner and B. J. Landry, *J. Org. Chem.*, 27, 1083 (1962).

(13) E. Berliner and J. C. Powers, *J. Am. Chem. Soc.*, 83, 905 (1961); E. Berliner, G. L. Zimmerman, and G. C. Pearson, *J. Org. Chem.*, 26, 1633 (1961).

(14) E. Berliner, F. J. Ochs, and G. L. Zimmerman, *ibid.*, 23, 495 (1958); and ref 10.

Table I. Kinetic Data for the Bromination of Hydrocarbons at 25°[a]

	Dependence of rate on bromide ion concentration				
NaBr, mole/l.	Fluoranthene[b]– 75% acetic acid $k_{obsd} \times 10^2$	Phenanthrene[c]– 75% acetic acid $k_{obsd} \times 10^3$	Pyrene[d]– 90% acetic acid k_{obsd}	1,2-Benz-anthracene[e]– 90% acetic acid k_{obsd}	Chrysene[f]– 90% acetic acid $k_{obsd} \times 10^2$
0.50	0.391	1.40	2.65	2.00	
0.40	0.515	1.73	3.50	2.71	
0.30	0.689	2.78	4.71	3.91	
0.25			6.08	5.21	
0.20	1.07	3.90	7.64	6.48	
0.15	1.47	5.13	10.9	8.28	
0.10	2.21	7.25	14.8		0.516
0.075					0.692
0.050					1.04
0.035					1.55
0.025					2.12

Dependence of rate on initial concentration of reactants[a,g]		
Pyrene × 10³, mole/l.	Bromine × 10³, mole/l.	k_{obsd}
1.144	0.967	2.60
1.144	0.510	2.74
1.144	0.246	2.53
1.148	0.937	2.76
2.452	1.935	2.57
2.452	0.967	2.70

[a] All rate constants are in l. mole^{-1} sec^{-1}. The total salt concentration was maintained at 0.5 *M* with $NaClO_4$ where necessary. [b] Fluoranthene 0.006–0.007 *M*, $Br_2 \simeq 0.002$ *M*. [c] Phenanthrene 0.009–0.012 *M*, $Br_2 \simeq 0.004$ *M*. [d] Pyrene 0.001–0.002 *M*, $Br_2 \simeq 0.001$ *M*. [e] 1,2-Benzanthracene 0.0012–0.0019 *M*, $Br_2 \simeq 0.0009$ *M*. [f] Chrysene 0.0006–0.0008 *M*, $Br_2 \simeq 0.0005$ *M*. [g] In 90% acetic acid, NaBr 0.50 *M*.

mine concentration do not change the second-order rate constant. The kinetic characteristics of bromination in 90% acetic acid are therefore identical with those in the more aqueous solvents. In Table I are listed the rate constants obtained on varying the bromide ion concentrations. When these were plotted according to eq 1, straight lines were obtained in every case, indicating that free bromine is the substituting agent in this solvent also. The plot for pyrene is shown in Figure 4.

According to eq 1, the straight lines should go through the origin. A small positive intercept would indicate some bromination by the tribromide ion.[15] Bromination by the tribromide ion has been observed in some cases,[10] notably in the reaction of very reactive substrates, such as amines or phenoxide ions.[16] In the case of the hydrocarbons, some of the plots afford very small, but negative, intercepts, which are not more than a few per cent of the slope. It is very likely that these intercepts are due to salt effects, and that they are of no mechanistic significance.[17] Their occurrence has no effect on k_2, the true rate constant for bromination by free bromine. But because of their occurrence, it is not safe to assess the relative rates of two compounds by merely comparing relative rates at a definite bromide ion concentration, which ought to be permissible if eq 1 held strictly. This would in principle be the simpler procedure, but even with very small but varying intercepts, discrepancies were noted, and the more tedious but safer method of evaluating k_2 for each compound separately was adopted. Nevertheless, the reactivity of anthracene even in 90% acetic acid is so great that, with our technique, its rate of reaction could only be studied at the highest bromide ion concentration and went to 75% completion in about 4 min. An average value of 12 runs at a 0.5 *M* bromide ion concentration was determined, and the relative rate of anthracene was found by comparing this value with that obtained for pyrene under the same conditions. For the reasons mentioned above, the value for anthracene is likely to be less accurate than the others.

Rate constants for bromination have now been determined in three different acetic acid solvent mixtures (50, 75, and 90%), and it is necessary for purposes of comparison to convert them all to the same solvent and temperature. They were all referred to 50% aqueous acetic acid at 25°. For naphthalene data are available in 50[10] and 75%[18] acetic acid, and the factor obtained from the ratio of rates was used to convert rates from 75 to 50% acid. 2,6-Dimethylnaphthalene is brominated 12.4 times faster in 75 than in 90% acetic acid.[19] With this factor, rates could be converted from 90 to 75% acetic acid. It must be emphasized that this involves the assumption that the relative rates do not vary with solvent composition, which is probably not exactly true. Checks with two other dimethylnaphthalenes show that the ratios obtained on going from 75 to 90% acetic acid are all of the same order of magnitude, and, in general, the factors on going from 50 to 75% acid (27.1) and from 75 to 90% acetic acid (12.4)

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(15) See the remarks in ref 10, footnote 21.

(16) R. P. Bell and D. J. Rawlinson, *J. Chem. Soc.*, 63 (1961); R. P. Bell and T. Spencer, *ibid.*, 1156 (1959); R. P. Bell and E. N. Ramsden, *ibid.*, 161 (1958).

(17) If the tribromide ion were to contribute to the total rate, the relation $k_{obsd}(K + Br^-) = k_2'K + k_2''(Br^-)$ should hold, and the expression on the left should increase with the bromide ion concentration. It actually slightly decreases in all cases. A similar observation was made by Bell and co-workers[16] and has been ascribed to a kinetic salt effect.

(18) Unpublished data of C. Chen, M.A. Thesis, Bryn Mawr College, 1963.

(19) E. Berliner, D. M. Falcione, and J. L. Riemenschneider, *J. Org. Chem.*, 30, 1812 (1965).

Table II. Rates of Bromination of Hydrocarbons in Aqueous Acetic Acids at 25°

Hydrocarbon	Acetic acid			Relative rate	Position of reaction	Partial rate factor
	50%	75%	90%			
Benzene[a]	2.74×10^{-6}			1	1	1
Biphenyl[a]	4.23×10^{-3}			1.54×10^{3}	4	4.34×10^{3}
Naphthalene[b]	3.41×10^{-1}	1.26×10^{-2}		1.24×10^{5}	1	1.84×10^{5}
					2	1.86×10^{3}
Phenanthrene		7.55×10^{-2}		7.43×10^{5}	9	2.23×10^{6}
Fluoranthene		2.34×10^{-1}		2.30×10^{6}	3	6.90×10^{6}
Chrysene			1.02×10^{-1}	1.25×10^{7}	6	3.75×10^{7}
Pyrene			2.33×10^{2}	2.84×10^{10}	1	4.26×10^{10}
1,2-Benzanthracene			2.00×10^{2}	2.44×10^{10}	7	1.46×10^{11}
Anthracene				7.87×10^{11}	9	2.36×10^{12}
2,6-Dimethylnaphthalene[c]		9.12	7.33×10^{-1}			
Acenaphthene[c]			4.50×10^{2}	5.49×10^{10}	5	1.65×10^{11}
Fluorene[d]		3.59×10^{-1}		3.53×10^{6}	2	1.03×10^{7}

[a] Reference 13. Rate constants were extrapolated from values at higher temperatures and the reported activation energies. [b] Reference 10 and 14. [c] Reference 19. [d] Reference 11.

are not great, compared to the over-all spread of rate constants. This procedure does, however, introduce an uncertainty in the final values, although the general consistency of the data makes it likely that it is not a great one.

The relative rates so calculated are listed in Table II. In order to compute partial rate factors from the relative rates, the isomer distribution in the bromination of each hydrocarbon has to be determined. This had previously been done for naphthalene,[10] biphenyl,[13] and fluorene[11] by the isotopic dilution method using Br^{82}. A combination of vapor phase chromatography and infrared spectroscopy was used in the present study for the remaining compounds. The identified monobromination products are 3-bromofluoranthene, 9-bromophenanthrene, 6-bromochrysene, 7-bromo-1,2-benzanthracene, 1-bromopyrene, and 9-bromoanthracene. In each case, only one isomer, corresponding to the one reported on preparative bromination, was detected. All were compared with authentic samples. In the cases of pyrene, fluoranthene, and phenanthrene, small amounts of disubstitution products (1 to 2%) were also present. Addition products (see below), detected or inferred in the bromination of phenanthrene and anthracene, are presumed to be formed after the rate-determining step and are not believed to affect the kinetically determined rate constants. There exists, of course, the possibility that under the gas chromatographic conditions employed and because of the instability of the columns at the high temperatures necessary for vpc analysis, isomeric substitution products were not resolved from the major components, or remained undetected in the infrared analyses. In the absence of the less common isomers for comparison purposes, the validity of the results can be assessed from products reported in analogous reactions. With the exception of fluoranthene, only one isomeric monosubstitution product has been reported in the preparative bromination of these hydrocarbons.[20] In the nitration of pyrene and chrysene, 1-nitropyrene and 6-nitrochrysene are formed predominantly; small amounts of another compound, probably an isomer of 6-nitrochrysene, are also present.[21] Anthracene is deuteriodeprotonated almost exclusively in the 9 position, and substitution in the 1 position, the next most reactive position, amounts to less than 0.2%.[5] Bromination by molecular bromine is more selective than either nitration or deuteriodeprotonation and would be expected to lead to even less isomer distribution. Although the bromination of fluoranthene in carbon bisulfide leads primarily to the 3 isomer, small but unspecified amounts of the 8 isomer have been reported.[22] No 8-bromofluoranthene, although small amounts of the 3,8-dibromo compound, could be detected in the present study, but the preparative bromination was conducted in the presence of PBr_3, which may well have made the bromine a less selective reagent. Because it is likely that other isomers *are* formed, in however small amounts, the partial rate factors reported in Table II must be considered to be maximum values, but it seems very unlikely that there could be significant errors involved in the values of the major components.

Additions Accompanying Substitution. In the 1930's Price outlined the general scheme by which addition may accompany aromatic substitution, and he concluded that both reactions involve a common carbonium ion intermediate.[23] Not much work was done on these reactions until recently, when de la Mare and co-workers, in a series of very thorough investigations, studied addition during chlorination of aromatic hydrocarbons in acetic acid and found that addition is rather common.[24] Because the bromo substitution products of phenanthrene and anthracene are commonly prepared from the addition compounds,[25] the occurrence of addition in the bromination of these two hydrocarbons was anticipated.

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(20) Pyrene: G. Lock, *Ber.*, 70, 926 (1937); chrysene: N. P. Buu-Hoi and J. Lecocq, *Compt. Rend.*, **226**, 87 (1948); 1,2-benzanthracene: G. M. Badger and J. W. Cook, *J. Chem. Soc.*, 409 (1940).

(21) P. M. G. Bavin and M. J. S. Dewar, *J. Chem. Soc.* 164 (1956); M. J. S. Dewar, T. Mole, D. S. Urch, and E. W. T. Warford, *ibid.*, 3572 (1956).

(22) J. von Braun and G. Manz, *Ann.*, **488**, 111 (1931); **496**, 170 (1932); R. Tobler, T. Holbro, P. Sutter, and W. Kern, *Helv. Chim. Acta*, **24**, 100E (1941); T. Holbro and E. Tagman, *ibid.*, **33**, 2178 (1950).

(23) C. C. Price, *J. Am. Chem. Soc.*, **58**, 1834, 2101 (1936); *Chem. Rev.*, **29**, 37 (1941).

(24) G. H. Beaven, P. B. D. de la Mare, M. Hassan, E. A. Johnson, and N. V. Klassen, *J. Chem. Soc.*, 2749 (1961); P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *ibid.*, 5285 (1961); G. H. Beaven, P. B. D. de la Mare, E. A. Johnson, and N. V. Klassen, *ibid.*, 988 (1962); P. B. D. de la Mare and R. Koenigsberger, *ibid.*, 5327 (1964); P. B. D. de la Mare, R. Koenigsberger, J. S. Lomas, V. Sanchez del Olmo, and A. Sexton, *Rec. Trav. Chim.*, **84**, 109 (1965).

(25) For instance, see the bibliography in C. A. Dornfeld, J. E. Callen, and G. H. Coleman, "*Organic Synthesis*," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 134; also E. de B. Barnett and J. W. Cook, *J. Chem. Soc.*, **125**, 1084 (1924).

The reaction products of phenanthrene and bromine in 75% acetic acid in the presence of sodium bromide were analyzed by vpc and infrared. They were found to consist of 9-bromophenanthrene, 9-acetoxyphenanthrene, 9,10-dibromophenanthrene, and phenanthrenequinone, all of which were identified by comparison with authentic samples. 9,10-Dibromo-9,10-dihydrophenanthrene was not detected in the products isolated, but the presence of 9-bromo-10-acetoxy-9,10-dihydrophenanthrene was inferred from the following evidence. The benzene-soluble fraction of the reaction mixture on gas chromatography yielded peaks corresponding to phenanthrene, 9,10-phenanthrenequinone, and small amounts of 9-bromo- and 9-acetoxyphenanthrene. The infrared spectrum of this fraction, before vpc analysis, contained all the bonds characteristic of acetates and the quinone, but the 870-cm^{-1} strong band characteristic of phenanthrene was missing. Phenanthrene must therefore be formed during vpc analysis, presumably in the heated injection port, and its identity after passage through the gas chromatograph was confirmed by the infrared spectrum of the condensed product. It appears then that a bromoacetoxy compound is present in the reaction products and decomposes on vpc analysis to phenanthrene, bromophenanthrene, and acetoxyphenanthrene. The possibility of the formation of 9,10-bromoacetoxy-9,10-dihydrophenanthrene by a substitution reaction on 9,-10-dibromo-9,10-dihydrophenanthrene was ruled out, because under the reaction conditions an authentic sample of the dibromo addition compound did not react with acetic acid. The dibromo addition compound could not be detected in the reaction mixture before distillation; a test with potassium iodide was negative under conditions when an authentic sample liberated iodine immediately. This is not quite conclusive, because the 9,10-dibromo-9,10-dihydrophenanthrene, if present, may decompose very rapidly to further products, and, if it should be the *cis* isomer, may not react sufficiently rapidly with KI for immediate detection. The 9,10-phenanthrenequinone is probably formed by oxidation of an addition product, perhaps a phenanthrol addition product. All reaction products can be accounted for by a two-step mechanism proceeding through a σ complex. Based on gas-chromatographic analysis of the isolated reaction products and excess hydrocarbon, all of the phenanthrene (102.7%) but only 49.5% of the bromine could be accounted for. Bromo-substitution products accounted for 21.1 wt % of the consumed bromine, of which 2.2% was 9,10-dibromophenanthrene; 9,10-bromoacetoxy-9,10-dihydrophenanthrene, whose presence was inferred, accounted for 5.1% of bromine, and phenanthrenequinone, assuming that it was formed through an addition compound, accounted for 23.3%. The low result in bromine may be due to the formation of further amounts of phenanthrene from addition products. In a recent study on the bromination of phenanthrene in methanol, a similar mixture of products was formed, except that methanol took the place of acetic acid as the nucleophile.[26]

The recovered reaction products of the reaction of anthracene and bromine in 90% acetic acid, in the presence of NaBr, were found to contain 9-bromoanthracene and 9-acetoxyanthracene. In some runs, depending on the procedure for work-up, anthraquinone and small amounts of 9,10-dibromoanthracene were also present.[27] In a typical run, 93.8% of the anthracene was accounted for, based on vpc analysis, 9-bromoanthracene accounted for 43.3 wt % of the bromine consumed, and 9-acetoxyanthracene, which is probably formed through a bromoacetoxy addition compound, accounted for 10% of bromine. It is possible that a substantial amount of 9,10-dibromo-9,10-dihydroanthracene is also formed and decomposed to anthracene, but the presence of 9-acetoxyanthracene comprises the main evidence for addition.

In the bromination of pyrene, 1,2-benzanthracene and fluoranthene, the substitution products accounted for over 90% of the bromine consumed, and addition products were not detected. Addition products are either not present at all or decompose so rapidly during the reaction or isolation that they have escaped our method of analysis. In the case of chrysene, the substitution product accounted for only 69.5% of the bromine. However, on the basis of a gravimetric determination of the separated reaction product and excess hydrocarbon, a theoretical yield was obtained. In principle, the relatively low amount of 6-bromochrysene could be due to the formation of an unstable addition product which could yield the unsubstituted hydrocarbon on vpc analysis or prior to it. However, by analogy with anthracene and phenanthrene, if addition accompanied substitution, some bromoacetoxy addition or substitution products would be expected. None were found in any of the cases, and the discrepancy between the gravimetric and vpc analyses for chrysene may be an artifact.

The present experiments establish that acetoxylation accompanies bromination of phenanthrene and anthracene, but not of the other systems. The acetoxy compounds must be formed by addition followed by elimination, but the bromo substitution products need not be.

The second-order rate constants given in the preceding section were determined by following the disappearance of bromine. The addition products are assumed to be formed after the rate-determining step, and the rate constants are not affected by addition. No irregularities in kinetic behavior, traceable to the incursion of addition, were ever noted. However, the partial rate factors in the 9 positions of anthracene and phenanthrene refer to the rate of attack of a bromine molecule in these positions, relative to one position in benzene, but not to the rate of formation of 9-bromophenanthrene or 9-bromoanthracene, relative to the formation of bromobenzene.

Although the kinetics of bromination of phenanthrene and of anthracene appear straightforward, the actual reaction for the formation of the various reaction products is considerably more complex than the kinetics indicate and warrants further investigation.

Discussion

The purpose of the study was to obtain experimental rate data on polynuclear aromatic hydrocarbons and

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(26) J. van der Linde and E. Havinga, *Rec. Trav. Chim.*, **84**, 1047 (1965).

(27) Anthraquinone has also been isolated from the bromination of anthracene in moist dioxane: C. C. Price and C. Weaver, *J. Am. Chem. Soc.*, **61**, 3360 (1939).

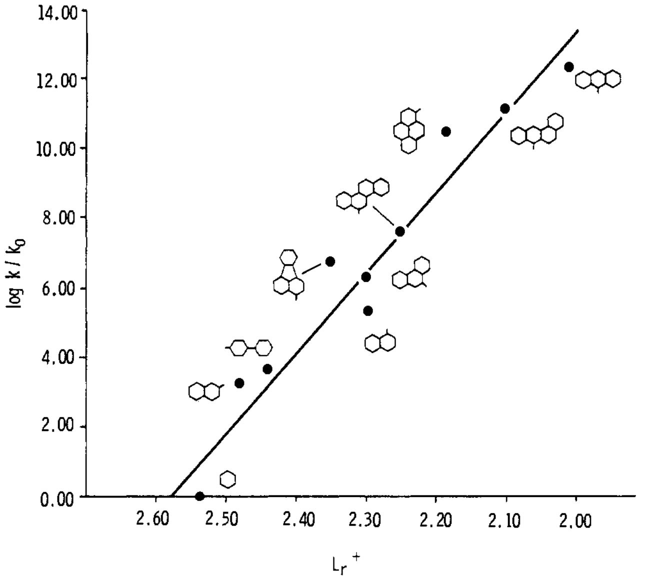

Figure 5. Correlation of rates of bromination with the index $L_r{}^+$.

to compare them with various reactivity parameters of the HMO method. There are a number of different reactivity indices which are in principle applicable to electrophilic aromatic substitution. Their meaning, and the methods of obtaining them, have been discussed in detail by Streitwieser.[28]

In relating the experimental data quantitatively to the theoretical indices, the usual assumption is made that changes in reactivity caused by structural variations are due only to changes in the π-electron energy, an assumption which is inherent in the Hückel treatment. Of the various reactivity indices, the localization energies, $L_r{}^+$, and their variants, are the most appropriate, because they explicitly take count of the transition state, or something which is considered to be very close to it.[29] This should certainly hold for bromination, which is known to have a very late transition state. A plot of the logarithms of partial rate factors against $L_r{}^+$ is shown in Figure 5, where the data for fluoranthene, the only nonalternant hydrocarbon, were not included in the least-square calculation. This graph is typical of all correlations, although there are minor variations where different indices are used. In Figure 5 the reactivities follow closely the theoretical predictions. In this correlation, as well as one with $L_r{}^\omega$, only one pair of hydrocarbons is reversed. Experimentally, the 9 position of phenanthrene is more reactive than the 1 position in naphthalene, but both compounds have the same $L_r{}^+$ for the most reactive positions, and $L_r{}^\omega$ predicts an even greater reactivity for naphthalene. The greater reactivity of phenanthrene than naphthalene is experimentally commonplace and has been observed in other substitution and various solvolytic side-chain reactions.[28] Almost all HMO indices predict the 12 position in 1,2-benzanthracene to be the most reactive whereas bromination takes place exclusively in the 7 position.[30] This is possibly the result of steric hindrance to the approach of the electrophile. The effective β for bromination, calculated from the slope of the line, is -31.4 kcal/mole.

In the plot of rate constants against Dewar's reactivity index, N_r, which is a perturbation approximation to localization energies, the slope of the correlation line is -11.8. The slopes for nitration, deuteriodeprotonation, and chlorination are -3.78, -5.40, and -10.6, respectively. From these values, β_x can be calculated; β_x has a meaning similar to Hammett's ρ value and is a measure of how closely the transition state resembles the Wheland intermediate.[31] For the three above-named reactions β_x is -4.7, -7.5, and -14.5 kcal/mole, while for bromination it is -16.1 kcal/mole.[32] This confirms that bromination has the latest transition state of those electrophilic substitution reactions for which sufficient data are available and is in agreement with the high ρ value for bromination of benzene derivatives.[33]

The experimental rate data also correlate reasonably well with those indices which refer to "isolated molecules" and which do not explicitly take into account the transition state and therefore refer to reactions with relatively unperturbed reactants. Of these, the free valency is a property of the ground state and is not a good model for aromatic substitution. Nevertheless, the correlation with bromination data is in the correct order but is slightly worse than that with the localization indices. This is also true of the correlation with the self-atom polarizabilities. It is a consequence of the fortuitous mathematical interrelation of the indices that when straight-line relations are obtained with one of them, equally good ones are usually obtained with all the others. This is a shortcoming of the theory, because the parameters often refer to quite different mechanisms of substitution, some with early and others with late transition states, but they cannot be used to differentiate between the mechanisms, except perhaps in the case of nonalternant hydrocarbons. Hence, bromination, which has a notoriously late transition state, gives reasonably good correlations with both localization and "isolated molecule" indices.

One of the primary deficiencies of the simple HMO method is the neglect of repulsion terms. Recently Dewar and Thompson calculated localization energies for electrophilic substitution by four modifications of the Pople method.[34] They are all variations of the SCF method, and two introduce electron correlation in addition to electron repulsion. In Figure 6 is shown the correlation with Dewar's localization energy L_{SPO}, calculated on the assumption that all bonds have a common aromatic length. The correlation with the L_{PPP} (common length) localization energies is similar. Dewar's treatment correctly predicts a higher reactivity for 9-phenanthrene than 1-naphthalene, which neither the $L_r{}^+$ nor the $L_r{}^\omega$ values do.[35] Biphenyl deviates from the line, but, as pointed out by Dewar, the assump-

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(28) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 11.

(29) E. Berliner, *Progr. Phys. Org. Chem.*, **2**, 253 (1964).

(30) The superdelocalizability, S_r,[28] predicts the 7 position in 1,2-benzanthracene to be more reactive than the 12 position.

(31) M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.*, 2789 (1956); 2946 (1957).

(32) A tentative value of -15.9 kcal/mole was obtained for β_x from a correlation with a smaller number of compounds.[29]

(33) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

(34) M. J. S. Dewar and C. C. Thompson, Jr., *J. Am. Chem. Soc.*, **87**, 4414 (1965).

(35) We thank Professor Dewar for making available the unpublished indices for the 7 position of 1,2-benzanthracene.

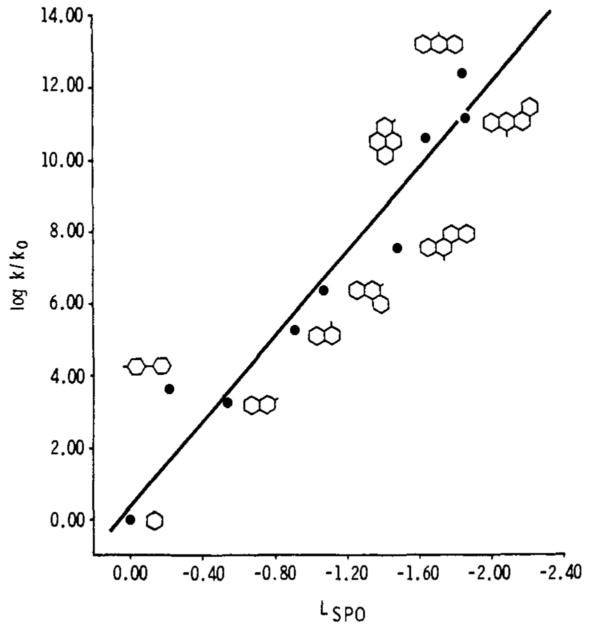

Figure 6. Correlation of rates of bromination with the index L_{SPO} (ev). β and C–C bond length fixed.

tion of equal bond lengths is not applicable to the pivot bond in biphenyl.

The success of the various correlations may be assessed by examining the errors in the slopes of the least-square correlation lines. This is perhaps not a very safe procedure, because the number of compounds is relatively small, and it does not necessarily reflect small reversals of reactivities or consistent deviations. The figures are presented in Table III.

Table III. The Correlation of Rates of Bromination with MO Indices and with Other Electrophilic Substitution Reactions

Index[a]	Least-square line		% probable error in slope	Average deviation of points from the line
	Slope	Intercept		
L_r[b]	−23.0	59.5	5.8	0.70
$L_r\omega$[b]	−16.8	27.6	5.4	0.71
N_r	−11.8	27.7	3.7	0.50
L_{SPO}[c]	−5.76	0.602	6.5 (4.8)[d]	0.80 (0.50)[d]
L_{PPP}[c]	−5.66	0.724	6.3 (4.5)[d]	0.78 (0.50)[d]
Z_r	27.7	−34.6	5.5	0.70
F_r	93.1	−35.4	8.6	1.0
π_{rr}	92.3	−34.7	8.4	0.97
Log K/K_0 HF equilibrium[e]	0.902	9.49	1.6	0.22
Log k/k_0 deuterio-deprotonation[f]	1.99	0.506	2.4	0.30
Log k/k_0 nitration[g]	2.38	0.374	4.8	0.46

[a] Reference 28. [b] Fluoranthene is not included. [c] Reference 34. β and C–C bond length fixed. [d] Biphenyl excluded. [e] Reference 6. [f] Reference 5. [g] Reference 4. Data for biphenyl were taken from Y. Mizuno and O. Simamura, *J. Chem. Soc.*, 3875 (1958), and for fluoranthene from A. Streitwieser, Jr., and R. C. Fahey, *J. Org. Chem.*, **27**, 2352 (1962).

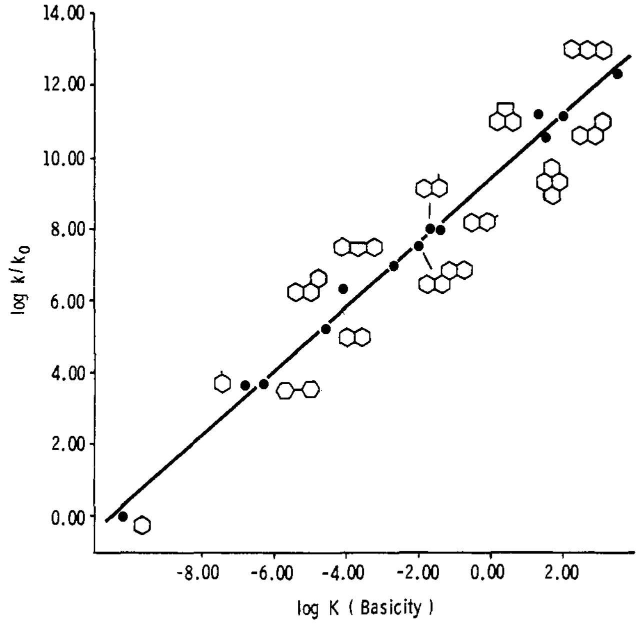

Figure 7. Correlation of rates of bromination with basicity constants.

All localization procedures give about equal results, the correlation with Dewar's reactivity numbers, N_r, having the smallest deviation as has been noted elsewhere.[28] The localization parameters correlate slightly better than those for the isolated molecules, and the free valency and self-atom polarizability give the poorest fit by this criterion. It should be stressed, however, that the correlation with all parameters must be considered satisfactory and that, as in many other correlations with experimental data on alternant hydrocarbon systems, the simple HMO method and its variations lead to quite acceptable results.

It was of further interest to compare the rate constants for bromination with other experimental quantities. The equilibrium $ArH + HF = ArHF^+ + F^-$, for which a large number of data are available,[6] has become the standard reaction for such comparisons and has been used to set up a $\sigma\rho$ scale for polynuclear hydrocarbons.[28] Several of the compounds for which bromination rates have been determined have saturated alkyl groups for which at present no generally useful MO parameters are available. They can, however, be included in the correlation with the basicity constants.[36] The correlation with the bromination rates is shown in Figure 7. Both reactions cover differences in reactivity of about 12 powers of ten, and the correlation is very good, in spite of the uncertainties in isomer distribution in the equilibrium reaction and the extrapolation of the bromination data from one aqueous acetic acid to another. The ρ value for the present correlation is 0.90 and those for the other electrophilic substitution reactions are: hydrogen fluoride equilibrium, 1; chlorination, 0.64; deuterio deprotonation, 0.47; and nitration, 0.26.[28] Bromination has a higher ρ (and β_x) than the other substitution reactions, corresponding to the low electrophilicity and high selectivity of molecular bromine, while the other reactions arrange themselves in the expected order, with nitration by the nitronium ion at the low end of the series.

When the rate constants for bromination are correlated with either rate constants for nitration or deuterio deprotonation, good correlation lines are also obtained. The experimental rate constants not only

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(36) Data for the methylnaphthalenes are from ref 18. The data for toluene are from the M.A. Thesis of P. A. Carney, Bryn Mawr College, 1960, and the Senior Honors Thesis of E. A. Sorrentino, Bryn Mawr College, 1958.

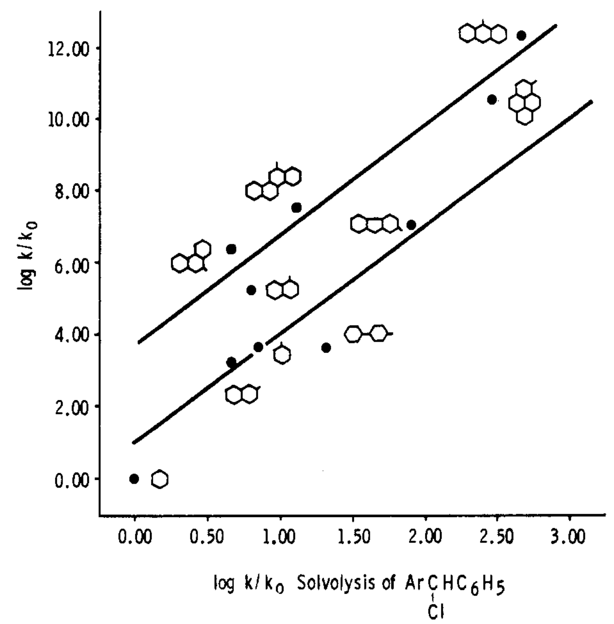

Figure 8. Correlation of rates of bromination with rates of solvolysis.

correlate well with each other, but, if the errors in the correlation lines are again taken as a criterion for the goodness of the fit (Table III), the correlations are slightly better than those with the theoretical parameters, which perhaps becomes significant in the correlation with the HF equilibrium.[37] This may indicate that relative reactivities of polynuclear aromatic systems are affected by factors, perhaps only to a minor extent, which are not incorporated in the theoretical indices, and may reflect the shortcomings in the basic assumptions which are made in the calculations and in the comparisons with experimental data.

The correlation of the experimental rate data was further extended to a comparison with electrophilic solvolytic side-chain reactions. The transition states of the two types of reaction have common features, and good correlations between solvolysis and substitution have been obtained in the benzene series.[33] In Figure 8 is shown the correlation between bromination rates and the rates of SN1 solvolysis of polynuclear arylphenylmethyl chlorides, $ArCHClC_6H_5$.[38] A similar graph is obtained in the correlation with the solvolysis of α-arylethyl chlorides, $ArCHClCH_3$.[39] The correlations are very poor. The compounds group themselves approximately into two classes; those with a 1-naphthalene-like structure react slower in the solvolytic reactions than anticipated from bromination rates. This could have been predicted, because in almost all correlations of solvolysis rates with HMO indices, the compounds fall on approximately two lines, with compounds in which the side chain is in a 1-naphthalene-like position on the low reactivity line.[28,31,38,39] This effect has been ascribed to steric hindrance either to solvation or to coplanarity in the 1 position of naphthalene. No such effect is observed in correlations of HMO indices with bromination data or other electrophilic substitution reactions, where the spatial demands are less stringent than when large side chains are present. It has recently been suggested that the occurrence of two lines on correlating solvolytic rates of polynuclear aromatic systems and HMO parameters is due to the deficiencies in the simple Hückel method and the neglect of electron-repulsion terms in the first-order treatment, and that only one line is obtained when the modified SCF indices are used.[34] In Figure 8, however, rates of substitution are correlated with rates of solvolysis, and the solvolysis reactions clearly deviate in the direction of a lowered reactivity for the 1-naphthalene-like compounds. This strongly suggests that the lower reactivity of 1-naphthalene-like compounds is real and inherent in these systems.

Experimental Section

Materials. All inorganic materials were best reagent grade chemicals. Sodium bromide and anhydrous sodium perchlorate were dried at 110° before use. Glacial acetic acid was purified by the procedure of Orton and Bradfield,[40] but it was found that one of the distillations could be omitted without affecting the purity of the acid. The modified procedure is as follows: to 5 l. of commercial acetic acid is added 30 g of chromic trioxide and 60 ml of acetic anhydride. The mixture is refluxed for 1 hr and then distilled, discarding head and tail fractions of about 400 ml each. The freezing point of the distillate was usually 16.4°, corresponding to 99.9% acetic acid. This was used as the "100%" acid. The 75 and 90% acetic acids were prepared by mixing appropriate volumes of thermostated acid and boiled-out water. Fresh batches were prepared periodically, and the kinetic data were found to be reproducible.

The hydrocarbons were commercial samples which were purified by recommended procedures. The purified hydrocarbons were analyzed by vpc, using a programmed temperature gas chromatograph (F & M Scientific Corp. Model 720) with a thermal conductivity detector. A 2 ft × 0.25 in. stainless steel column packed with 5% by weight of Carbowax 20M on 80–100 mesh Diatoport S was found to be efficient in separating the major components from the impurities. The hydrocarbons had the following purities: fluoranthene, mp 110.7–111.4°, 98.6 wt %; phenanthrene, 99.6–100.3°, 99.5%; 1,2-benzanthracene, 159.6–160.4, 98.7%; pyrene, 149.6–150.3°; chrysene, 257.5–258.5°; anthracene, 217.0–218.2°. No impurities could be detected in the last three compounds.

The major bromination products were prepared and purified according to literature procedures. We encountered considerable difficulties in preparing pure bromopyrene and bromochrysene. The crude materials in the bromination of pyrene in CCl_4 contained pyrene, monobromo-, and a small amount of dibromopyrene. Recrystallizations from ethanol were followed by vpc, and although pyrene could be removed by repeated crystallizations, the amount of the less soluble dibromopyrenes increased. The following procedure was finally adopted. The twice-crystallized product was dissolved in a small amount of benzene, filtered from less soluble material, and the product remaining in the filtrate was again recrystallized from ethanol. It melted at 94.8–95.8° (lit.[20] 95°) and consisted of 1 wt % pyrene, 93.7% 1-bromopyrene, and 5.3% dibromopyrene. Since the composition of the sample was thus known, it served as a suitable standard for vpc of the kinetic reaction products. The dibromo product, prepared with twice the amount of bromine, showed only one major component, and the isomeric dibromo products were not resolved. The more insoluble 1,6-dibromopyrene melted at 229–231° (lit. 221–222°). An attempt to obtain the 1,8 isomer from the combined mother liquors was not successful. We could not brominate chrysene with bromosuccinimide.[20] The benzene-crystallized product from the bromination of chrysene in nitrobenzene was analyzed by a gas chromatographic standard addition method and found to contain 84.2 wt % of bromochrysene, 15.8% of chrysene, and a trace of a dibromochrysene. Attempts at further purification by recrystallization were unsuccessful. The mixture was separated on a 2-ft, silicon rubber column, and 2-bromochrysene of mp 153.6–155.0° (lit.[20] 152°) was obtained in small amounts. Similarly, 9-bromoanthracene, prepared from anthracene dibromide by heating,[41] consisted of 4.6 wt % of

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(37) However a larger number of compounds was correlated with the HF equilibrium than with the other two reactions.

(38) L. Verbit and E. Berliner, *J. Am Chem.. Soc.*, **86**, 3307 (1964).

(39) E. Berliner and N. Shieh, *ibid.*, **79**, 3849 (1957).

(40) K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 983 (1927).

(41) E. de B. Barnett and J. W. Cook, *ibid.*, **125**, 1084 (1924).

anthracene, 87.4% of bromoanthracene, and 8% of 9,10-dibromoanthracene.[42] Commercial 9-bromoanthracene also consisted of these three components. The melting points and purities of the other products were 3-bromofluoranthene, 103–105° (lit.[22,43] 103–105°, 110°), 98%; 3,8-dibromofluoranthene, mp 203–206° (lit.[27] 205°); 7-bromo-1,2-benzanthracene, mp 147.6–148.8° (lit.[20] 147.5–148.5°); 9,10-dibromoanthracene, 226.3–227.3° (lit.[44] 226°), 99%; 9-acetoxyanthracene, 132.0–134.5° (lit.[45] 133–134°), 90%; 9-bromophenanthrene, 64–65° (lit.[46] 64–65°), 99%; and the unstable 9,10-phenanthrene dibromide, 74–84° (lit.[26] 60–80°).[47] In an attempt to detect monobromination products other than 3-bromofluoranthene, the residue from kinetic runs, as well as synthetic materials and concentrated mother liquors, were subjected to vpc on several columns (SE 30, Apiezon L, polyphenyl). A 4 ft × 0.25 in. o.d. column containing a mixed stationary phase of 1% Apiezon L and 1% Bentone 34 on 80–100 mesh Diatoport S, which resolved completely a mixture of 1- and 2-bromonaphthalene, was tried, but 3-bromofluoranthene was not eluted at 200° and higher temperatures could not be used because of the thermal instability of Benton 34. Only 3-bromofluoranthene was obtained in all trials.

We are grateful to Professor de la Mare of Bedford College of the University of London for a pure sample of 9-acetoxyphenanthrene, and to Dr. S. Mallory for a pure sample of phenanthrenequinone.

Kinetic Determinations. The kinetic measurements were carried out as described before.[10–12] The concentration of hydrocarbons was always in excess of that of bromine. Depending on the reactivity of the compound, reactions were allowed to proceed to from 50 to 90% completion. The bromination of pyrene, anthracene, and benzanthracene is so fast that the initial bromine concentration was determined from a blank. In some runs, the initial titer of the blank differed by a few per cent from the value calculated from the intercept of the second-order plot. In those cases, the initial concentrations were calculated from the intercept. It was found from blank runs that the loss of bromine due to volatilization was negligible.

Rate constants were obtained graphically from plots according to the second-order rate equation. All runs were conducted at least in duplicate. The average rate constants listed in Table I had average deviations from the mean which ranged from 1.3 to 3%, except for the very fast reaction of anthracene, when it was 6.2%. In the bromination of phenanthrene a yellow reaction product (phenanthrenequinone?) obscured the end point in the slower runs, but satisfactory end points were obtained on addition of 2 ml of benzene. K for the tribromide ion equilibrium was taken as 0.0110 mole/l. in 75%[48] and 0.0073 mole/l. in 90%[49] acetic acid, respectively.

Product Analyses. The conditions of a typical kinetic run were reproduced for the product analysis. All runs were conducted in duplicate on a 100-ml scale; 200-ml samples were used for phenanthrene. The initial bromine concentrations were obtained from blanks. After a minimum of ten half-lives, the reaction mixtures were diluted with 50 ml of water and extracted four times with 30-ml portions of petroleum ether. The petroleum ether extract was washed with water to remove acetic acid. In the case of phenanthrene, some petroleum ether insoluble material (mainly phenanthrenequinone) was extracted with benzene. The solvent was evaporated on a steam bath, and the residue, consisting of reaction product and excess of hydrocarbon, was dried under vacuum and weighed. The recovery of the extracted material was always between 95 and 100% of the calculated values. The residues were redissolved in benzene (2 ml) for gas chromatography. For the separation of the reaction products of the bromination of phenanthrene and anthracene 6 ft × 0.25 in. o.d. columns of silicon gum rubber SE 30 on 80–100 mesh Diatoport S were found suitable, while for all other compounds 2 ft × 0.25 in. columns were used. The infrared spectra were recorded in chloroform or carbon tetrachloride (in a KBr disk for the reaction products of chrysene) on a Perkin-Elmer Infrachord Model 137. Reaction products were identified by comparisons of the spectra and retention times with those of authentic samples. All absorption bands in the infrared could be accounted for by the components identified from retention time data. In the quantitative determinations, the vpc peak area responses were related to concentrations by calibrations with mixtures of known composition. For all details see the Ph.D. dissertation of L. Altschuler.

In the product analysis of phenanthrene, both the petroleum ether and benzene extracts, redissolved in acetone, gave negative tests on addition of KI; under the same conditions authentic phenanthrene dibromide gave a strong positive test.

A sample of phenanthrene dibromide, dissolved in 100 ml of 75% acetic acid, was allowed to stand at room temperature for 1 week. The petroleum ether extract showed no carbonyl absorption (no acetoxy group present). A gas chromatogram of the phenanthrene dibromide indicated that it decomposes to a mixture of 9-bromophenanthrene and phenanthrene in a ratio of 2:1.

In the case of anthracene, slightly different proportions of products were obtained, depending on whether the petroleum ether extract was removed by gentle heating on the steam bath (a), or by vacuum distillation at room temperature with a slow passage of air through a capillary (b), or whether it was evaporated at room temperature overnight (c). In the last case, anthraquinone and traces of two unidentified products which were present in residues separated by procedures a and b were not present; these are probably formed during the work-up. Only data obtained by procedure c are reported in the text.

Acknowledgment. This work was supported by National Science Foundation Grants G-19755 and GP-4986, which are gratefully acknowledged. We also acknowledge stimulating discussions with Professor P. B. D. de la Mare.

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(42) See also W. E. Bachmann and M. C. Kloetzel, *J. Org. Chem.*, **3**, 55 (1938).

(43) N. Campbell and R. S. Gow, *J. Chem. Soc.*, 1555 (1949).

(44) I. M. Heilbron and J. S. Heaton, "*Organic Synthesis*," Coll. Vol. I, John Wiley and Sons, Inc., New York, N.Y., 1941, p 207.

(45) R. C. Fuson and D. E. Brasure, *J. Am. Chem. Soc.*, 77, 3131 (1955).

(46) C. A. Dornfeld, *et al.*, in ref 25.

(47) All melting points are corrected.

(48) A. E. Bradfield, G. I. Davies, and E. Long, *J. Chem. Soc.*, 1389 (1949).

(49) Estimated by extrapolation of the data of T. W. Nagakawa, L. J. Andrews, and R. M. Keefer, *J. Phys. Chem.*, **61**, 1007 (1957).