Experimental Section

The instrumentation and procedures of chemical ionization mass spectrometry have been described elsewhere.[2a]

Methylthiomethyl acetate and methylthiomethyl propionate were prepared by allowing dimethyl sulfoxide to react with acetic anhydride and propionic anhydride, respectively (Pummerer reaction).[15] Each was purified by preparative gas chromatography. Physical constants and spectral data agreed with literature[16] values.

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Rates of Protodetritiation of Polycyclic Aromatic Hydrocarbons in Trifluoroacetic Acid[1]

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Abstract: Rates are reported for some or all of the positions of naphthalene, biphenylene, benzo[*b*]biphenylene, phenanthrene, chrysene, pyrene, fluoranthene, triphenylene, and perylene for protodetritiation in 96.9% trifluoroacetic acid–3.1% perchloric acid at 25° and in 98% trifluoroacetic acid–2% carbon tetrachloride at 70°. The results are compared with related results from Eaborn's research group and the two solvent systems are interrelated. The result is an extensive set of quantitative relative reactivities for aromatic substitution on polycyclic aromatic hydrocarbons suitable for testing various molecular orbital methods.

Aromatic substitution reactions and their orientation for specific positions in aromatic hydrocarbons have long been useful for testing theories of organic chemistry such as resonance theory and molecular orbital methods. Electrophilic hydrogen isotope exchange is an especially simple and convenient type of aromatic substitution and in the form of protodedeuteration or protodetritiation is particularly important because quantitative reactivities can thus be obtained for positions too unreactive for measurement by direct substitution.[3] Such protodetritiations were pioneered by Eaborn's research group, first in mixtures of trifluoroacetic acid with strong mineral acid such as perchloric acid at room temperature[4] and subsequently in trifluoroacetic acid alone at 70°.[5] Because of our own interest in applying molecular orbital methods to quantitative reactivities in aromatic substitution, we have applied Eaborn's approach to additional polycyclic aromatic hydrocarbons, first in a mixture of 96.9% trifluoroacetic acid–3.1% perchloric acid at 25° (I) and subsequently in trifluoroacetic acid at 70° (II). In this paper we summarize the results we have obtained for both solvent systems. These results taken together with the data of Eaborn allow a quantitative correlation of the two solvent systems and provide reactivity data for many individual positions of a wide variety of polycyclic aromatic hydrocarbons.

The tritiated hydrocarbons were generally prepared by treatment of the known bromo derivatives with butyllithium followed by quenching of the aryllithium with tritiated water. Most of the kinetic runs were worked up with the LSKIN program of DeTar and DeTar[6] or by Perrin's program.[7] The results are summarized in Table I and are discussed by individual systems as follows.

Naphthalene. The rate reported by Bott, Spillett, and Eaborn[8] for naphthalene-1-*t* in trifluoroacetic acid at 70° is 20% higher than our results. Our solvent generally contained about 2% of carbon tetrachloride in order to provide increased solubility for the higher polycyclic hydrocarbons. In Table II we summarize the effect of several solvent variations. It is seen that a small amount of water causes a substantial increase of rate whereas carbon tetrachloride has essentially no effect. Hence, the discrepancy of 20% still remains and is disconcerting because it would appear to lie outside the combined limits of experimental error. However, the discrepancy is not important compared with the total range of reactivity of 10^4 measured in this work.

Phenanthrene. Our runs with solvent system I complement the results of Eaborn's group with trifluoroacetic acid at 70°.[9] We did not do the 4 position because of potential steric hindrance effects but for the remaining positions we obtain the same order of reactivity: $9 > 1 > 3 > 2$. Dewar and Warfield[10] obtained this same order in nitration of phenanthrene. The comparison of our results with Eaborn's helps to interrelate the two trifluoroacetic acid solvent systems (*vide infra*).

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(2) National Science Foundation Postdoctoral Fellow, 1963–1964.

(3) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, Amsterdam, 1965, Chapter 8.

(4) C. Eaborn and R. Taylor, *J. Chem. Soc.*, 247 (1961).

(5) R. Baker, C. Eaborn, and J. A. Sperry, *ibid.*, 2382 (1962).

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Table I. Rates for Protodetritiations

	—System I,[a] 25.0°—		—System II,[b] 70.0°—	
Hydrocarbon-*t*	10^5k, sec^{-1}	No. of runs	10^5k, sec^{-1}	No. of runs
1-Naphthalene	35	2[c]	0.915 ± 0.014	2
2-Naphthalene	5.6	1[d]	0.126 ± 0.006	2
1-Biphenylene	4.8[e]	1		
2-Biphenylene	321[e]	1		
5-Benzo[*b*]biphenylene	392	1		
1-Phenanthrene	29.7 ± 0.6[f]	3		
2-Phenanthrene	5.6 ± 0.5[f]	2		
3-Phenanthrene	9.4 ± 0.4[f]	2		
9-Phenanthrene	52.5 ± 0.9[f]	2		
6-Chrysene			9.15 ± 0.32	2
1-Pyrene			4.6 ± 0.3[g]	2
			17.8 ± 0.1[h]	2
			66.0 ± 0.8[i]	1
			163 ± 3[j]	2
2-Pyrene	2.75	1	0.074 ± 0.003	2
4-Pyrene	31	1	1.28 ± 0.05	2
1-Fluoranthene			0.273 ± 0.015	2
2-Fluoranthene			0.067 ± 0.001	1
3-Fluoranthene			8.40 ± 0.20	2
1-Triphenylene	31.6 ± 0.9[d,k]	3		
2-Triphenylene	5.76 ± 0.07[d,k]	4		
	5.91 ± 0.22[k]	2		
3-Perylene			7.7 ± 0.8[g]	1

[a] 96.9% CF_3COOH, 3.1% of 70% $HClO_4$; $H_0 = -6.44$; 25.0°. [b] 98.04% CF_3COOH, 1.96% CCl_4; 70.0°. [c] One each of protodetritiation and tritiodeprotonation gave the same rate constant. [d] Tritiodeprotonation. [e] Tritiodeprotonation gave $k(1-) = 4.3 \times 10^{-5}$; $k(2-) = 275 \times 10^{-5}$ sec^{-1}. [f] Different batch of solvent; $H_0 = -6.51$. [g] Solvent was 70% CF_3COOH–30% CCl_4; $H_0 \cong 4.5$; 25°. [h] 25.00 ± 0.02°. [i] 40.00 ± 0.04°. [j] 50.00 ± 0.02°. [k] Solvent contained 5-10% CCl_4.

Table II. Effect of Solvent Variations on Protodetritiation of Naphthalene-1-*t* at 70°

Addend[a]	10^5k, sec^{-1}
None	0.937 ± 0.022
1.96% CCl_4	0.915 ± 0.014
1.94% CCl_4, 0.97% H_2O	1.05 ± 0.03
1.94% CCl_4, 0.97% $(CF_3CO)_2O$	0.878 ± 0.024

[a] [Naphthalene] = 0.0015 *M*.

Perylene. Perylene is known to be an extremely reactive hydrocarbon. On bromination it gives directly a mixture of 3,9- and 3,10-dibromide.[11] Treatment of the dibromide with butyllithium followed by tritiated water gave perylene-3-*t*. Solutions in trifluoroacetic acid surprisingly gave no exchange. Perylene has low solubility in trifluoroacetic acid and these solutions were extremely dilute. Further examination showed that the solutions have the spectrum of the radical cation reported by Dallinga.[12] These solutions have an esr spectrum but this spectrum was not resolved.[13] Lewis and Singer[14] have also reported the production of radical cation from the hydrocarbon and antimony pentachloride. In our case the radical cation is probably produced in these dilute solutions by reaction of the protonated hydrocarbon with dissolved oxygen (see pyrene below). Because of the relatively large number of positions that can be protonated in perylene plus the expected large primary isotope effect for reaction of the protonated hydrocarbon with oxygen, the resulting perylene radical cation has substantially the same tritium content as the starting hydrocarbon. On quenching, the hydrocarbon is regenerated with little consequent loss of tritium.

By using larger amounts of carbon tetrachloride in the solvent mixture the solubility of perylene was increased and exchange rates were measured. Pyrene-1-*t* was measured in the same solvent to obtain a relative rate that could be used for comparison with other systems.

Pyrene. All electrophilic aromatic substitution reactions on pyrene give only the 1-substituted product. The unique value of protodetritiation is demonstrated with this hydrocarbon for determining the relative reactivities of the other two positions. The tritiated pyrenes have been described earlier.[15] Pyrene-1-*t* is so reactive that the protodetritiations were carried out in trifluoroacetic acid at lower temperatures and extrapolated up to 70°. The activation parameters obtained are $\Delta H^* = 16.3 \pm 0.03$ kcal/mol and $\Delta S^* = -21.2 \pm 0.1$ eu. The exchange rate of pyrene-4-*t* was obtained in the normal way but the exchange rate of pyrene-2-*t* was so low that the normal techniques resulted in decomposition. Using vacuum line techniques and a reaction vessel used in our "Acidities of Hydrocarbons" research,[15] the exchange reaction in the absence of air gave good first-order kinetics over a period of 11 days. The relative rates of the 1, 2, and 4 positions of, respectively, 1.0×10^4, 1.0, and 17.3, demonstrate why only substitution products in the 1 position are isolated.

Although the oxygen-free procedure was not applied to perylene, it seems quite likely that such techniques would avoid the incursion of radical cations and should be generally applicable to reactive hydrocarbons.

Triphenylene. Electrophilic aromatic substitution reactions with triphenylene generally give a 2-substituted product. Examples are Friedel–Crafts acylation and sulfonation.[16] It should be noted that the 1 position is of the 4-phenanthrene type and is expected to be highly hindered. Bazin and Dewar[17] in nitration of triphenylene obtained equal amounts of both mononitro derivatives and, consequently, suggested that the 1 position is apparently the more reactive; such an order of reactivity agrees with molecular orbital calculations. Dallinga and coworkers[18] with deuterodeprotonation in a trifluoroacetic acid–carbon tetrachloride–sulfuric acid mixture obtained a relative reactivity of the two positions of 3.1 and assumed the 1 position to be the more reactive. The tritiodeprotonation kinetics in system I was dissected into two first-order rate constants[19] of 31.6×10^{-5} sec^{-1} and 5.76×10^{-5} sec^{-1}, a relative reactivity of 5.5. 2-Bromotriphenylene was prepared as described previously,[16] and converted to triphenylene-2-*t* which gave a rate constant for protodetritiation of 5.91×10^{-5}. This

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result confirms the previous predictions that the 1 position of triphenylene is the more reactive and that the predominance of 2 products is undoubtedly a result of steric hindrance.

Fluoranthene. This hydrocarbon is important because it is a nonalternant benzenoid system. We had previously looked at nitration of this hydrocarbon and found a relative reactivity order of 3 > 8 > 7 > 1 > 2.[20] In our present study we examined only the 1-, 2-, and 3-tritiated fluoranthenes because during our study Bancroft[21] indicated his interest in studying this system. The partial reactivity order found in the present work, 3 > 1 > 2, agrees with the previous nitration studies.

The combined results from the present work and those of Eaborn are summarized in Table III for these two solvent systems as rates relative to naphthalene-1. These relative rates correlate excellently with each other with the least-squares correlation equation given in eq 1.

Table III. Comparison of Protodetritiations in $CF_3COOH-HClO_3$ at 25° (System I) and CF_3COOH at 70° (System II)

Symbol	Hydrocarbon	System I Rel rate	System II Rel rate	Rel rate for nitration[g]
B	Benzene		0.0010[a]	0.0021
1N	1-Naphthalene	(1.00)	(1.00)	(1.00)
2N	2-Naphthalene	0.160	0.138	0.106
1P	1-Phenanthrene	0.74	0.934[a]	0.77
2P	2-Phenanthrene	0.140	0.179[a]	0.196
3P	3-Phenanthrene	0.23	0.399[a]	0.64
4P	4-Phenanthrene		0.84[a]	0.168
9P	9-Phenanthrene	1.31	1.67[a]	1.04
1Bi	1-Biphenylene	0.131[b]	0.107[c]	
2Bi	2-Biphenylene	8.6[b]	14.5[c]	
6C	6-Chrysene		10.0	7.4
1Py	1-Pyrene		806	36
2Py	2-Pyrene	0.079	0.081	
4Py	4-Pyrene	0.89	1.40	
1F	1-Fluoranthene		0.30	0.7[h]
2F	2-Fluoranthene		0.073	
3F	3-Fluoranthene		9.2	2.9[h]
1T	1-Triphenylene	0.91	1.06[d,e]	1.3
2T	2-Triphenylene	0.166	0.17[d,e]	1.3
3Pe	3-Perylene		1400[f]	164

[a] Reference 9. [b] See also reference 19. [c] J. M. Blatchly and R. Taylor, *J. Chem. Soc.*, 4641 (1964). [d] Not included in least-squares eq 1. [e] Extrapolated from system I with eq 1. [f] Estimated from relative rate of 1-pyrene in $CF_3COOH-CCl_4$ at 25°. [g] In acetic anhydride at 0–25° (ref 22). [h] In acetic anhydride at 0° (ref 20).

$$\log \text{rel } k_{II} = (1.089 \pm 0.05) \times \log k_I + (0.089 \pm 0.03) \quad (1)$$

This equation was used to extrapolate triphenylene reactivities to system II. The result is an extensive set of reactivity data on polycyclic aromatic hydrocarbons suitable for application of molecular orbital calculations. Such molecular orbital treatments are discussed in the next paper.

The most extensive previous set of reactivities available for MO correlations was based on nitration[22] and is more limited in number of aromatic positions studied, is less sensitive to structure, and is more subject to steric hindrance perturbations. The nitration results are also summarized in Table III.

It has been shown repeatedly that electrophilic aromatic substitution reactions, especially those with low steric requirements, generally correlate mutually.[23] The simplicity of the reaction and the extensive data now available make the protodetritiation reaction an ideal standard for such correlations. Three such correlations are summarized in Table IV. The correlations are summarized in Table IV. The correlations are all quite good; deviations that do occur generally occur only in hindered positions and are in the expected direction.

Table IV. Correlations of Protodetritiation with Other Electrophilic Aromatic Substitution Reactions

Reaction	Slope ± std dev[a]	Intercept ± std dev	Corr coeff
Deuterodeprotonation[b]	1.08 ± 0.10	0.12 ± 0.16	0.978
Nitration[c]	1.28 ± 0.10	0.19 ± 0.11	0.964
Bromination[d]	0.54 ± 0.03	−0.06 ± 0.08	0.994

[a] Protodetritiation as ordinate. [b] In a $CF_3COOD-CCl_4-D_2SO_4$ solvent (ref 18). Similar protodedeuteration work in a $CF_4COOH-H_2O-HClO_4$ mixture gives a slope of about 1.2 for fewer points (C. Parkanyi and R. Zahradnik, *Tetrahedron Lett.*, 1897 (1963)). [c] Table III. [d] L. Altschuler and E. Berliner, *J. Amer. Chem. Soc.*, **88**, 5837 (1966).

Finally, electrophilic aromatic substitution reactions on substituted benzenes have been shown by Brown and Okamoto[24,25] to correlate well with σ^+ constants. Such correlations have been criticized;[26] hence, it is of interest to compare the present set of protodetritiation reactivities with the set of σ^+ constants for polycyclic aromatic rings derived from acetolysis reactivities of arylmethyl tosylates.[27] These data are plotted in Figure 1 and are found to give a good linear correlation except for two points. Benzene itself does not fit the other systems and suggests that the data may be best fitted by a curve.[28] Benzene is relatively unreactive in trifluoroacetic acid and there might be some question of the accuracy of its relative protodetritiation reactivity; however, it fits well in the correlations of protodetritiations with other aromatic substitutions in Table IV and its rate cannot be seriously in error. Its deviation from linearity in Figure 1 is clearly real. The curvature found in the present case, if general, may mean that polycyclic cations, in which charge delocalization is an important stabilizing mechanism, should not be considered in the same sense as substituted systems in which charge-substituent dipole electrostatic effects constitute an important interaction mechanism. Such

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

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

(26) Reference 3, Chapter 11.

(27) A. Streitwieser, Jr., H. A. Hammond, R. H. Jagow, R. M. Williams, R. G. Jesaitis, C. J. Chang, and R. Wolf, *J. Amer. Chem. Soc.*, **92**, 5141 (1970).

(28) In this respect, note ref 23, p 378.

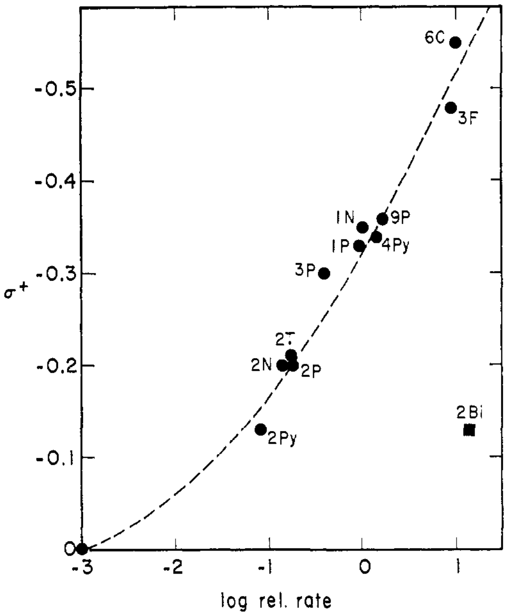

Figure 1. Comparison of protodetritiation reactivities of polycyclic aromatic hydrocarbons with σ^+ values for corresponding arylmethyl cations. The dotted curve is just a smooth curve through the data. The symbols for hydrocarbons are identified in Table III.

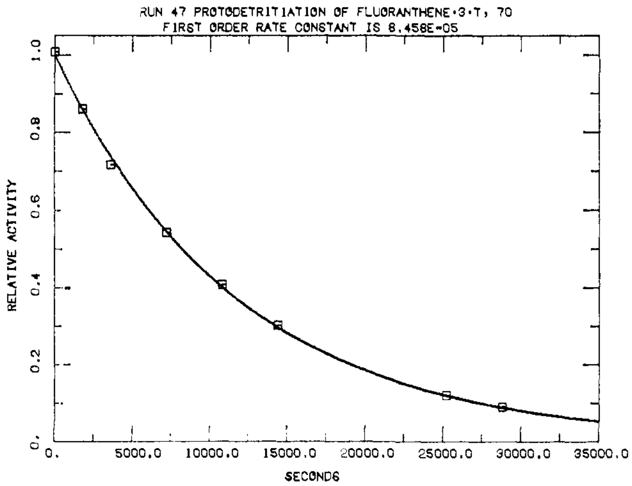

Figure 2. Typical protodetritiation kinetic run. This example is a direct CalComp plot for fluoranthene-3-*t* at 70°. The curve is the calculated curve for the rate constant given (8.458 × 10^{-5} sec^{-1}).

a distinction has emerged from recent SCF calculations of aromatic cations.[27]

Finally, our value for σ^+ of 2-biphenylenemethyl cation, −0.13,[27] is far lower in magnitude than protodetritiation reactivity would require. Figure 1 would suggest a value of about −0.55 to −0.6, not far from the σ^+ value of −0.625 derived by Blatchly and Taylor.[29] More study is clearly required of the relative stabilities of biphenylenylmethyl cations.

Experimental Section

Tritiated Hydrocarbons. Several of the tritiated arenes were prepared in an earlier study.[15] The labeled materials were generally prepared by treating the appropriate bromoarene with butyllithium in ether followed by quenching with excess tritiated water. Unlabeled hydrocarbon was added to the mixture, isolated and sublimed, or recrystallized. Activities were measured by scintillation counting and were generally about 10^6 dpm/mg. The following preparation is illustrative.

Fluoranthene-2-*t*. After standing for 5.5 min, a solution of butyllithium and 13 mg (0.046 mmol) of 2-bromofluoranthene in 10 ml of ether was quenched with 20 μl of tritiated water. The residue was mixed with 300 mg of fluoranthene (Rütgerswerke) and recrystallized from aqueous ethanol to give 180 mg of small white flakes, mp 109.8–110.5° (lit.[30] mp 110°), specific activity 1.2 × 10^6 dpm/mg.

The bromoarenes used are known compounds with one exception; the bromonaphthalenes are commercial products, small samples of 1-bromo- and 3-bromophenanthrene were kindly sent by Professor L. Pichat, and 2-bromophenanthrene, mp 94.5–95° (lit.[31] 95–96°), was prepared from the amine with the Sandmeyer reaction.[32] 6-Bromochrysene, mp 151.8–153.5° (lit.[33] 152°), was prepared in low yield from the amine[34] and the general Sandmeyer conditions of Badger and Stephens.[35] A mixture of 3,9- and 3,10-dibromoperylene was prepared by bromination of perylene[36] and was used directly; because of the tracer quantities of tritium used, metallation of the dibromoarene and quenching gives a monotritiated hydrocarbon. 2-Bromotriphenylene, mp 132.5–133.5° (lit.[16] 132–133°), was prepared by bromination of triphenylene.[16] 2-Bromofluoranthene, mp 101–103° (lit.[37] 102–104°), was prepared[38] from the amine and the Sandmeyer reaction.[31] 3-Bromofluoranthene, mp 102–103° (lit.[39] 110°), was prepared by bromination of 1,2,3,10b-tetrahydrofluoranthene followed by dehydrogenation.[39]

1-Bromofluoranthene has not been reported. Its preparation follows.

1-Bromofluoranthene. 1-Nitrofluoranthene was prepared by nitration of 1,2,3,10b-tetrahydrofluoranthene followed by dehydrogenation following Campbell and Wilshire.[40] A suspension of 2.5 g (10.1 mmol) in 250 ml of absolute ethanol was hydrogenated over 10% Pd/C. The filtered solution had uv absorption at 225, 260, 285, 312 (shoulder), 326, and 405 nm. Addition of HCl produced a spectrum closely resembling that of fluoranthene. The free amine decomposes rapidly and was kept in solution under nitrogen and isolated as the hydrobromide, mp 290–295° dec. This salt was suspended in 200 ml of water and 5 ml of concentrated HBr, and maintained at 3° during the introduction with stirring of a solution of 0.9 g of sodium nitrite in 10 ml of water. A solution of 2.9 g of curpous bromide in 50 ml of 41% HBr and 50 ml of water was added to the orange suspension of the diazonium salt. The mixture was heated for 9 hr, cooled, and filtered. The product was chromatographed several times in CCl_4–$CHCl_3$ or CCl_4 on neutral alumina and silica gel to give 200 mg of yellow needles of 1-bromofluoranthene, mp 100–103°.

Anal.[41] Calcd for $C_{16}H_9Br$: C, 68.35; H, 3.23; Br, 28.42. Found: C, 67.85; H, 3.25; Br, 28.80.

Kinetics. The trifluoroacetic acid used was obtained from Matheson Coleman and Bell and from the Columbia Chemical Co. The acid was fractionated from an equivolume mixture with concentrated sulfuric acid, collecting a fraction bp 72°. Samples were treated periodically with silver trifluoroacetate to test for halides but these tests were always negative. In early runs the acid was kept in glass-stoppered bottles with samples syringed out as needed. Later the acid was kept in an all-glass system under nitrogen with aliquots removed using nitrogen pressure and a burette.

Solvent I. Solvent I was prepared by diluting 31 ml of 70% perchloric acid to 1 l. with trifluoroacetic acid. The H_0 of the solution was determined to be −6.51 using 2-bromo-4,6-dinitro-

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(41) Analysis by Chemical Analysis Services Laboratory, College of Chemistry, University of California, Berkeley, Calif.

aniline (pK_a −6.68[42]). For each kinetic run a 55-ml aliquot of solvent I was syringed into a 100-ml long-necked flask, sealed with a serum cap, and maintained at 25.00 ± 0.02°. A solution of the hydrocarbon in 2 ml of CCl_4 was injected into the flask and shaken vigorously. At intervals, 10-ml aliquots were withdrawn and quenched with excess cold 2 *N* NaOH. The mixture was extracted with ether or cyclohexane, washed until neutral, and dried. In early runs the evaporated residues were sublimed but this procedure gave irreproducible results; subsequent control experiments showed that sublimation resulted in loss of tritium activity. Hence, the extracts were assayed spectrophotometrically and the samples for counting were prepared by diluting known volumes with scintillation solution.

Solvent II. A solution of 2–8 mg of tritiated hydrocarbon in 0.5 ml of CCl_4 was injected into 25 ml of trifluoroacetic acid and 8 aliquots were sealed in 5-ml ampoules with nitrogen flushing. The ampoules were maintained at 70.00 ± 0.06°; after thermal equilibrium was reached, points were removed at intervals and quenched in Dry Ice–acetone. The contents were worked up as above.

In the runs with pyrene-2-*t* the solutions were made up with vacuum line techniques and transferred with argon pressure to tubes which were sealed off with complete exclusion of air. For best results we recommend this type of procedure generally for studies of polycyclic hydrocarbons in trifluoroacetic acid. In several runs using the earlier procedures we noticed varying amounts of decomposition that probably result from radical cations produced by oxygen.

The data were handled as first-order kinetics using Perrin's program[7] or LSKIN[8] and were checked for quality with CalComp plots. A typical plot is shown in Figure 2.

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Semiempirical SCF MO Calculations on Electrophilic Aromatic Substitution[1]

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Abstract: Various semiempirical MO methods have been applied to the extensive reactivity data now available from protodetritiation of polycyclic aromatic hydrocarbons in trifluoroacetic acid. In common with past experience the simple HMO method is totally inadequate to handle the wide range of structures available. The HMO-ω technique, however, is astonishingly satisfactory, undoubtedly because it is an approximation of SCF-π methods. The latter methods are also satisfactory and do not depend in an important way on the specific model or parameter set used. The CNDO/2 method also gives a generally excellent correlation. The effect of methyl substituents is well accounted for by CNDO/2 although the resulting correlation differs from that of the unsubstituted polycyclic systems. None of the methods gives a satisfactory account of the strained biphenylene system; CNDO/2 also is useless in interpreting aromatic substitution reactivities in fluorene and benzocyclobutene.

Studies of protodetritiation of polycyclic aromatic hydrocarbons in trifluoroacetic acid pioneered by Eaborn and his research group[2,3] and extended by us[4] have provided data for many positions of a number of compounds covering a reactivity range of over six orders of magnitude. These data are unique because quantitative reactivity data are available not only for those positions normally reactive in aromatic substitution reactions but also for several positions which are too unreactive to be accessible in direct reactions—examples are the pyrene-2 and fluoranthene-2 positions; hence, these data are ideal for comparisons with molecular orbital models. Furthermore, the mechanism has been elucidated with adequate detail,[5] and has been shown to involve the formation of a symmetrical Wheland intermediate. The transition states leading to and from the intermediate are almost identical, differing only by the isotope effect of tritium and hydrogen. Problems such as free-radical formation[6] and oxidation[4] can be largely circumvented by use of pure trifluoroacetic acid[2] and careful technique.[4]

In this paper we apply several MO models to these data. First we review the use of the simple Hückel (HMO) method followed by the SCF methods: Pople's SCF-π method and the all-valence-electron CNDO/2 procedure.

HMO

Much has already been published on the HMO treatment of aromatic substitution.[7] Of the many indices proposed to determine reactivity in aromatic substitution the localization energy appears to be the most fundamental and reliable. Dewar's reactivity numbers, a perturbation approach to localization energies,[8] apply only to alternant systems; hence in order to include the nonalternant system, fluoranthene, cation localization energies, L_r^+, were used as determined from the usual HMO calculations. The HMO

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