

## Electrophilic Aromatic Substitution. Part 18.<sup>1</sup> Protiodetritiation of Anthracene, Coronene (Dibenzo[*ghi,pqr*]perylene), and Triphenylene in Anhydrous Trifluoroacetic Acid †

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A method is described for determining aromatic hydrogen exchange rates in anhydrous trifluoroacetic acid for aromatic hydrocarbons of very low solubility. Kinetic runs, carried out on as little as 0.05 mg of aromatic compound, lead to the following partial rate factors (positions in parentheses): anthracene, 7 900(1); 1 135(2);  $1.27 \times 10^7$ (9); coronene, 7 400(1); triphenylene, 620(1); 136(2). The corresponding  $\sigma^+$  values are -0.445, -0.35, -0.81, -0.44, -0.315, and -0.24. This, the first quantitative determination of the electrophilic aromatic reactivity of anthracene, shows that the 1- and 2-positions are more reactive than the corresponding positions in naphthalene, but these positions are closer in reactivity than are those in naphthalene. Both effects are predicted by calculations which also correctly predict the reactivity of triphenylene and coronene; the exchange results confirm that the nitration of triphenylene gives anomalous rate data.

PROTIODETRITIATION of tritium-labelled aromatic hydrocarbons in trifluoroacetic acid at 70° is the standard method for measuring rates of hydrogen exchange of carbocyclic aromatic compounds, and the largest body of quantitative data for electrophilic aromatic substitution is available for reactions carried out under this condition.<sup>2</sup> However, despite the many advantages of the reaction and these conditions, there remains the disadvantage that trifluoroacetic acid is a poor solvent (though of course good relative to most acids). Consequently measurements of rates of exchange of insoluble aromatic compounds have not been made under this condition. Thus for example, the quantitative electrophilic reactivity of anthracene, one of the simplest polycyclic aromatics, has never been determined in this (or indeed in any other) electrophilic aromatic substitution. Some approximate reactivity data were described by Dallinga *et al.* for this and other polycyclics using a range of sulphuric acid-trifluoroacetic acid-carbon tetrachloride mixtures as the exchange media.<sup>3</sup> However, subsequent determinations for some of the other compounds gave partial rate factors which were at least seven-fold greater,<sup>4,5</sup> and it seems unlikely that these differences merely reflect differences in the exchange conditions; accurate determination of the rates of exchange of anthracene in anhydrous trifluoroacetic acid was therefore desirable. This is important not only

because of the relationship to naphthalene and phenanthrene, both of which are fully documented,<sup>4,6</sup> but also because of the relationship to [14]annulenes and benzanthracenes which are important from their aromaticity and carcinogenic aspects respectively. We therefore undertook a study of anthracene, and also of triphenylene and coronene; the latter provided a particularly severe test of our method for dealing with insoluble aromatic compounds.

### RESULTS AND DISCUSSION

Rate coefficients, obtained by the method described in the Experimental section, could be duplicated to within  $\pm 2\%$  and are given in the Table. Because of the high

Rate coefficients for detritiation of Ar<sup>3</sup>H in CF<sub>3</sub>CO<sub>2</sub>H at 70 °C and derived  $\sigma^+$  values

ArH	Position of <sup>3</sup> H	10 <sup>7</sup> k/s <sup>-1</sup>	$\sigma^+$
Anthracene	1	730	-0.445
	2	108	-0.35
	9	$121 \times 10^4$ †	-0.82
Triphenylene	1	58.8	-0.315
	2	13.0	-0.24
Coronene	1	700	-0.44

† Derived from the rate at 25 °C of  $327 \times 10^{-5} \text{ s}^{-1}$  (see text).

reactivity of the 9-position of anthracene, its rate could not be measured at temperatures significantly in excess of 25 °C, nor much below this because of the solubility

<sup>3</sup> G. Dallinga, A. A. Verrijn Stuart, P. J. Smit, and E. L. Mackor, *Z. Elektrochem.*, 1957, **61**, 1019.

<sup>4</sup> C. Eaborn and R. Taylor, *J. Chem. Soc.*, 1961, 1012.

<sup>5</sup> A. Streitwieser, A. Lewis, I. Schwager, R. W. Fish, and S. Labana, *J. Amer. Chem. Soc.*, 1970, **92**, 6525.

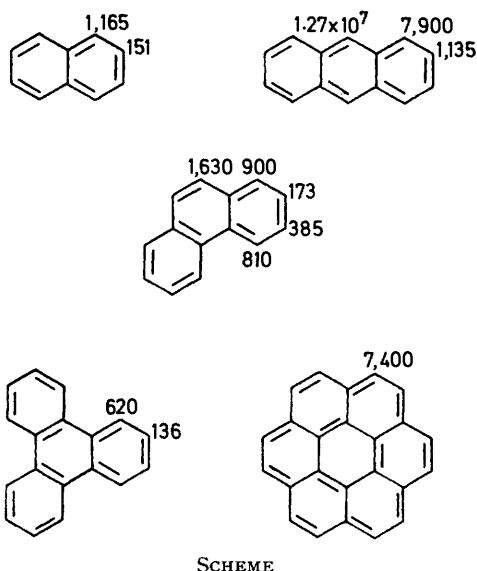
<sup>6</sup> K. C. C. Bancroft, R. W. Bott, and C. Eaborn, *J.C.S. Perkin II*, 1972, 95.

† No reprints available.

<sup>1</sup> Part 17, M. M. J. Le Guen and R. Taylor, *J.C.S. Perkin II*, 1976, 559.

<sup>2</sup> Ref. 1 and earlier papers in this series; R. Baker, C. Eaborn, and R. Taylor, *J.C.S. Perkin II*, 1972, 97; R. Taylor, 'Comprehensive Chemical Kinetics,' Elsevier, Amsterdam, 1972, vol. 13, Table 159.

problem. However the more soluble acenaphthene exchanges at the 5-position at a similar rate at 25 °C ( $9\,500 \times 10^{-7} \text{ s}^{-1}$ ) with an activation energy of 17.1 kcal mol<sup>-1</sup>.<sup>7</sup> Since steric effects are normally insignificant in hydrogen exchange, rates of exchange are directly related to activation energies, and we may calculate by means of the Arrhenius equation a value of 16.35 kcal mol<sup>-1</sup> for anthracene. This gives a rate at 70 °C of 0.121 s<sup>-1</sup>, a partial rate factor of  $1.27 \times 10^7$ , and  $\sigma^+ = -0.81$ . It should be noted that an error of 1.0 kcal mol<sup>-1</sup> in the calculated activation energy produces an error in  $\sigma^+$  of only 0.01, so our estimated value of the latter cannot be significantly in error. The derived partial rate factors are set out in the Scheme along with those for some related molecules.<sup>4,6</sup>



Notable features are the following.

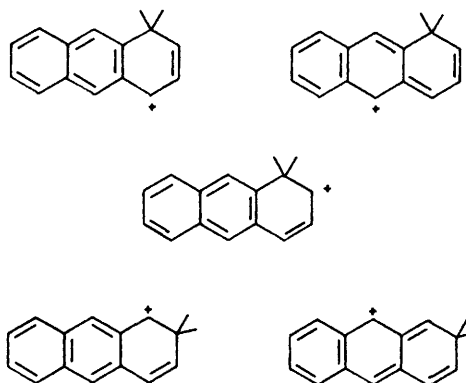
(i) *Anthracene*.—The reactivity of the 9-position could be assumed from additivity to be predicted (very approximately) by the square of the activating effect of a 2:3-benzo substituent. This latter (see naphthalene) is 1 165, so the predicted partial rate factor is  $1.5 \times 10^6$ , reasonably close to the observed value. In fact localization energies (calculated by the Hückel method), Dewar numbers, and CNDO/2 calculations<sup>8</sup> all predict that the 9-position of anthracene should be slightly greater than the square of the effect of the 2:3-benzo substituent, as we observe.

The 1- and 2-positions are each more reactive than the corresponding positions in naphthalene, as also predicted by the above theoretical methods. The reactivity difference between these two positions is however smaller than in naphthalene. This arises from the fact that whereas in the resonance hybrid for the Wheland intermediate for substitution in naphthalene,

<sup>7</sup> H. V. Ansell and R. Taylor, *Tetrahedron Letters*, 1971, 4915.

<sup>8</sup> A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, p. 336; A. Streitwieser, P. C. Mowery, R. G. Jesaitis, and A. Lewis, *J. Amer. Chem. Soc.*, 1970, **92**, 6529.

one and two structures retain benzenoid character for 2- and 1-substitution respectively, in anthracene there are two such structures for 2-substitution and three for 1-substitution (Figure). Consequently although



Principal canonical forms for substitution at the 1- and 2-positions of anthracene

each of these positions should be more reactive than the corresponding positions in naphthalene, the numerical ratio of favoured structures for 1- relative to 2-substitution is diminished in anthracene.

Our partial rate factors for the 1-, 2-, and 9-positions may be compared with those obtained by Dallinga *et al.*,<sup>3</sup> viz. 891, 178, and  $1.29 \times 10^6$ . Once again therefore their values are low by a factor of 7–10 fold. Their results are consistent however in that they also found a smaller reactivity difference between the 1- and 2-positions than between the corresponding positions in naphthalene.

Recently, Eaborn *et al.* have measured the partial rate factor for protodesilylation of the 9-position of anthracene ( $1.1 \times 10^6$ ).<sup>9</sup> This showed that an earlier recorded<sup>10</sup> and abnormally low value of 4.1 must be in error and probably referred to reaction at either the 1- or 2-position. Our results indicate that this value relates to substitution at the 2-position, since calculation of it from the exchange data for the 2-position of anthracene and naphthalene, and the desilylation value of 2.16 for the latter,<sup>10</sup> indicates that a value of ca. 3.5 should be obtained.

(ii) *Coronene*.—The only previous measurement of the reactivity of coronene, in nitration, showed it to be rather greater in reactivity than the 1-position of naphthalene or the 9-position of phenanthrene, and this is true also in exchange.

(iii) *Triphenylene*.—The partial rate factors which we observe are some 20-fold greater than those obtained by Dallinga *et al.*<sup>3</sup> Streitwieser *et al.*<sup>5</sup> measured the reactivity of triphenylene and found, as we do, that it is comparable with that of naphthalene. No partial rate factors could be determined from their work as the exchange was carried out under conditions different to

<sup>9</sup> C. Eaborn, R. Eidenschink, and D. R. M. Walton, *J. Organometallic Chem.*, 1975, **96**, 183.

<sup>10</sup> R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965, p. 240.

those used for other standard aromatic compounds, owing to the solubility problem. However, their 1:2-reactivity ratio of 5.5 at 25 °C is in good agreement with our value of 4.55 at 70 °C since the reactivity difference could be expected to decrease with increasing temperature. (By contrast, Dallinga *et al.* obtained a value of 3.1 at 30°.) The reactivity ratio of 4.55 is less than the ratio of the reactivities of the 1- and 2-positions in both naphthalene and anthracene, and this is predicted by localization energies, Dewar numbers, and CNDO/2 calculations.<sup>8</sup> Our results also show that triphenylene is less reactive at both positions than the 1-position of naphthalene or the 9-position of phenanthrene, and this result is paralleled in halogenation.<sup>11</sup> [The latter gave equal reactivities for the 1- and 2-positions, though steric hindrance to 1-substitution (*peri*-naphthalene-like) would account for this.] By contrast, nitration of the 1- and 2-positions of triphenylene (found to be equally reactive) was reported as taking place more readily than at the 1-position of naphthalene and the 9-position of phenanthrene.<sup>12</sup> Dewar has subsequently reported that his results may be 200% in error:<sup>13</sup> this is the indication of our data.

**Correlation with Reactivity Parameters.**—The data obtained in this study, taken along with those for naphthalene, give satisfactory correlations with either Dewar numbers, or localization energies, calculated by the Hückel or CNDO/2 methods; the respective correlation coefficients are 0.955, 0.957, and 0.984. The latter was obtained excluding coronene, since the calculated parameter is not available because of the large amount of computer time required for a molecule of this size.

#### EXPERIMENTAL

[1-, 2-, and 9-<sup>3</sup>H]Anthracene.—The preparation of these compounds has been described.<sup>14</sup>

[1-<sup>3</sup>H]Coronene.—A mixture of coronene (9 mg), benzene (1 ml), trifluoroacetic acid (1 ml), and tritiated water (0.025 ml of 500 mCi ml<sup>-1</sup> activity) was heated in a sealed ampoule at 140 °C during 7 days. Extraction and work up of the product, involving recrystallisation and column chromatography gave [1-<sup>3</sup>H]coronene. This contained a persistent active contaminant which was however unreactive towards exchange, so the kinetic runs were corrected for the presence of this active background in the usual way.

[1,2-<sup>3</sup>H<sub>2</sub>]Triphenylene.—A mixture of triphenylene (50 mg), trifluoroacetic acid (10 ml), 72% perchloric acid (*ca.* 0.1 ml), and tritiated water (0.02 ml of 500 mCi ml<sup>-1</sup> activity) was heated under reflux during 12 h. Extensive decomposition took place, but work up gave a 20% yield of [1,2-<sup>3</sup>H<sub>2</sub>]triphenylene of 0.8 MCi g<sup>-1</sup> specific activity. Kinetic studies were carried out on this doubly labelled compound in the usual way, the observed kinetic plots being resolved into two first-order components. The faster rate was attributed to reaction at the 1-position, this having been shown to be correct by Streitwieser *et al.*<sup>5</sup>

<sup>11</sup> Ref. 10, pp. 220—221.

<sup>12</sup> Ref. 10, p. 88.

**Kinetic Methods.**—Our usual technique for carrying out kinetic studies in anhydrous trifluoroacetic acid is to add *ca.* 10 ml of the acid to *ca.* 5—30 mg of the aromatic compound at room temperature, shake for *ca.* 10 min and pipette *ca.* 1 ml samples into ampoules which are then sealed and placed in the thermostat bath at 70 °C. However, it has been our experience that when using this method with very insoluble aromatic compounds, scatter is obtained on the resultant kinetic plots evidently because each ampoule contains a different amount of aromatic compound. This is true even when the 'solution' appears to be perfectly homogeneous, and true also if the 'solution' is filtered through a sinter before dividing into the ampoules. We reasoned that very small particles must be present in the mixture which are both invisible to the naked eye and small enough to pass through a sinter.

Our modification of this technique consists of dissolving the aromatic in a good solvent having a b.p. >80 °C and dividing this solution into the ampoules as before. The ampoules are warmed, and the solvent removed by a stream of dry nitrogen. Trifluoroacetic acid is then added to each ampoule which is sealed as before. In this way, each ampoule contains exactly the same amount of aromatic and although this may not completely dissolve in the acid at room temperature it does so at the higher temperature employed in the kinetics. Shaking of the sealed ampoule prior to placing them in the bath helps reduce the time required for solution of the aromatic at the bath temperature. Complete homogeneity of the samples is indicated not only by the excellent linearity of the first-order kinetic plots, but also by the fact that progressive reduction of the concentration of aromatic compound taken for the kinetic runs produces no detectable variation in the derived rate coefficients.

Since there is effectively no limit to the specific activity which can be incorporated into the aromatic compound, it is possible to work with very low concentrations of the latter. For coronene, the total amount of aromatic used in each run was *ca.* 0.05 mg, *i.e.* 5 µg in each ampoule (10 ampoules per run). Obviously the techniques can only be used with involatile aromatic compounds (these happen to be the most insoluble ones) and a good criterion of suitability is to see if the sample has a perceptible odour; if it does it is unsuitable.

In view of the increasing cost of trifluoroacetic acid we have developed a method for recovering this from the kinetic runs. The alkaline layers, obtained when the ampoules are crushed in alkali under the layer of scintillator, are removed, neutralized, and allowed to evaporate to dryness. Vacuum evaporation with heating is uneconomic, but solar-wind evaporation is very suitable (the activity of the tritiated water removed is insignificant). After a final heating to dryness at 100° (to remove any water of crystallisation and hence any residual activity) excess of sulphuric acid is added and pure inactive trifluoroacetic acid can be recovered by fractional distillation.

We thank the S.R.C. for financial support of this work.

[6/1072 Received, 6th June, 1976]

<sup>13</sup> M. J. S. Dewar, 'The Molecular Orbital Theory of Organic Chemistry,' McGraw-Hill, New York, 1969, p. 297.

<sup>14</sup> R. Taylor, G. J. Wright, and A. J. Homes, *J. Chem. Soc. (B)*, 1967, 780; R. Taylor, *Tetrahedron Letters*, 1975, 435.