Electrophilic Aromatic Substitution. Part 31.[1] Partial Rate Factors for Detritiation of Thieno[2,3-*b*]thiophen and Thieno[3,2-*b*]thiophen: Weak Hydrogen Bonding to Sulphur in Trifluoroacetic Acid

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Thieno[2,3-*b*]thiophen (I) and thieno[3,2-*b*]thiophen (II), specifically labelled with tritium in each position have been prepared, and their rates of protiodetritiation measured along with that for thiophen in either pure trifluoroacetic acid, or mixtures of trifluoroacetic acid and acetic acid, all at 70 °C. The dependence of exchange rate coefficients upon acid composition indicates that the ring sulphur is hydrogen bonded, and to an extent which depends upon the number of sulphur atoms in the heterocycle. Partial rate factors for detritiation of the non-hydrogen-bonded compounds are calculated as follows (position and compound in parentheses): 7.18×10^8 [2-(I)]; 6.83×10^8 [2-(II)]; 9.75×10^7 (2-thiophen); 7.59×10^5 [3-(I)]; 5.54×10^5 [3-(II)]; 7.84×10^4 (3-thiophen), the corresponding σ^+-values being −1.012, −1.010, −0.913, −0.672, −0.656, and −0.560. The results, taken along with those for acylation and chlorination show that (II) is more polarisable than (I), so that these compounds, like all other π-excessive heterocycles previously examined, are unsuitable for rigorous application of the Extended Selectivity Relationship. Annelation of thiophen by thiophen produces a comparable change in reactivities of the α- and β-positions in contrast to annelation by benzene, where the high resonance energy of benzene plays a crucial role in raising the reactivity of the β-position, relative to that of the α-position.

THE electrophilic reactivities of π-excessive heterocycles containing a single heteroatom (*e.g.* furan, thiophen, benzo[*b*]thiophen, *etc.*) have been thoroughly investigated.[2] From these studies it is clear that it is difficult to define quantitatively the reactivity of a given position because of the high polarisability of the molecules, in the same way that it is difficult to ascribe a single σ^+-value to a highly polarisable substituted benzene such as anisole. Thus the Extended Selectivity Relationship cannot be applied to these molecules with any real success, *i.e.* the spread of σ^+-values derived from different reactions is large [2] (and is of course a natural consequence of the Reactivity–Selectivity Principle). Previous work showed that the positions which are the most polarisable are in fact those which are usually the least reactive, *i.e.* the β-positions of furan and thiophen, and the α-positions of benzo[*b*]furan and benzo[*b*]thiophen.[2] Thus for example the 2-position of benzo[*b*]furan becomes increasingly reactive relative to the 3-position as the demand for resonance stabilisation of the reaction increases, and even overtakes it in reactivity. This is also correctly predicted by calculations, because π-electron densities (appropriate to a reaction with an early transition state and low demand for resonance) predict the reactivity order 3 > 2, whereas localization energies (late transition state, high demand for resonance) predict the order 2 > 3.

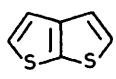
There have by contrast been very few studies of the electrophilic reactivities of heterocycles containing two or more heteroatoms, especially when the heteroatoms are in different rings. Data, mostly qualitative, have been obtained for azaindoles,[3] naphthyridines,[4] phenanthrolines,[5] benzo[1,2-*d*:3,4-*d*']di-imidazoles,[6] triazacycl-[3,3,3]azines,[7] imidazo[2,1-*b*]thiazole,[8] thienopyridines,[9] thieno[2,3-*d*]pyridazines,[10] furo[2,3-*c*]pyridine,[11] benzodithiophens,[12] thienobenzothiophens,[13] selenopheno-[3,2-*b*]selenophen,[14] selenopheno[3,2-*b*]thiophen,[14] and benzothieno[3,2-*b*]benzothiophen.[15] Some quantitative data have been obtained for the thienothiophens, *e.g.* thieno[2,3-*b*]thiophen (I) and thieno[3,2-*b*]thiophen (II).[16-18] The data for the thienothiophens from different reactions disagree with each other as shown by the relative reactivities which are given along with the reactivities relative to thiophen (III) in Table 1. This shows the following points.

TABLE 1

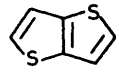
Relative reactivities in electrophilic substitution

	Thiophen		(I)		(II)		2-(I)
Reaction	2-	3-	2-	3-	2-	3-	2-Thiophen
Acetylation	200	1	634	6.3	594	4.8	3.17
Dedeuteriation	1 235 [a]	(1) [a]	9 630		8 770		7.8
Chlorination	250	1	5 975	23.9	8 300	< 8.3	23.9
Formylation	> 1 000	1	> 34 000	~68	> 44 400	not detected	34

[a] This ratio is from a previous study for detritiation.[25]



(I)



(II)

(III)

(i) The 3-position of (I) appears to be more reactive than that of (II). This is only implied for chlorination and formylation, since no products for 3-substitution of

(II) were detected. Data for the 3-positions were not obtained in hydrogen exchange.

(ii) The relative reactivities of the 2-positions of (I) and (II) are inconsistent in that the order 2-(I) > 2-(II) in acetylation and dedeuteriation is the opposite of that for the other reactions.

(iii) The results are inconsistent because the order of relative reactivities of the 2- and 3-positions of thiophen does not parallel the order for the reactivities of the 2-position of thiophen relative to the 2-position of (I) [or (II), not shown].

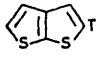
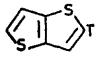
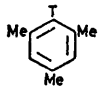
The present work was therefore undertaken in order to: (i) obtain accurate partial rate factors for hydrogen exchange (detritiation), and to obtain these for both 2- and 3-positions; (ii) determine σ^+-values for each position so that as other data becomes available the accuracy of the Extended Selectivity Relationship for predicting the reactivity of these compounds can be assessed; (iii) provide data for comparing the reactivities of higher homologues; (iv) compare the observed reactivities with those predicted; and (v) assess the effect of hydrogen bonding. Oxygen-containing aromatics are quite strongly hydrogen bonded in trifluoroacetic acid.[19-21] Thus for example f_p^{OMe} is only 1.9×10^5 compared with 6.4×10^6 predicted from its σ^+-value and the ρ-factor (−8.75) for detritiation in trifluoroacetic acid. Secondly, the activation energy for detritiation of [4-^{3}H]anisole is greater than that for the less reactive [4-^{3}H]thioanisole.[20] Thirdly, and most importantly with regard to the present work, the decrease in exchange rate on going to media containing increasing amounts of acetic acid is less than for other compounds, because the extent of hydrogen bonding diminishes in this direction. This is true for other methoxy-containing aromatics.[21] One could expect therefore that hydrogen bonding to sulphur-containing compounds would also occur, but to a lesser extent, but no previous study of this has been made.

RESULTS AND DISCUSSION

Rate coefficients for detritiation of (I)—(III) in various trifluoroacetic–acetic acid media are given in Table 2, along with those previously determined for [4-^{3}H]-anisole and [^{3}H]mesitylene.[22]

TABLE 2

Rate coefficients (10^7 k/s^{-1}) for detritiation in CF_3CO_2H–HOAc mixtures [a]

Aromatic	% CF_3CO_2H in HOAc (v/v) 100	75	50	35	25	15
	*5.7 × 10⁶*		42 650	5 810	1 430	350
	*5.5 × 10⁶*		41 500	5 370	1 340	333
	2.2 × 10⁶		7 400	910	210	47.5
	6.75 × 10⁵		1 674	129	21.1	3.45
	1.7 × 10⁴			23.7		1.89
	5.8 × 10³	977	45	*6.13*		*0.37*
	4.4 × 10³	742	32	*4.36*		*0.27*
	1 780					*0.0384*

[a] Italicised values are extrapolated from the rate–acidity profiles of the other position in the same molecule.

The following are notable features of the results.

(i) The compounds have different rate–acidity profiles. Thus the relative rates between 100% CF_3CO_2H and 35% CF_3CO_2H–65% HOAc are: 5 230 (mesitylene), 2 420 (thiophen), 950 (thienothiophens), and 717 (anisole). These factors do not parallel reactivities, so the differences are not due to a selectivity effect. The lower

the factor the greater the degree of hydrogen bonding, and thus anisole gives the smallest value. However, the values for thiophen and the thienothiophens are considerably less than that for mesitylene which suggests that the sulphur-containing compounds are also hydrogen bonded. Moreover, the factor is smaller for the thienothiophens (which contain two sulphur atoms) than for thiophen (with only one), and this provides firm support for hydrogen bonding as the cause. (We shall subsequently show that the factor is even smaller for dithienothiophens, which contain three sulphur atoms). We assume hydrogen bonding to sulphur reduces the availability of the lone pair for resonance with the π-electrons of the ring.

(ii) From the rate coefficient for exchange of [4-^{3}H]-anisole in 35% CF_3CO_2H–65% HOAc, and that estimated for [^{3}H]benzene under the same conditions,[22] we may calculate $\sigma^+_{4\text{-OMe}}$ as −0.706 which is substantially less than the standard value of −0.778.[23] (The standard σ^+-values usually apply quite well to detritiation in CF_3CO_2H.) Consequently there is still substantial hydrogen bonding in this medium and it cannot be used to determine the reactivities of the sulphur-containing aromatics. In 15% CF_3O_2H–85% HOAc a similar calculation gives $\sigma^+_{4\text{-OMe}}$ −0.76, sufficiently close to the standard value to indicate that hydrogen-bonding in this medium is trivial. We therefore require rate coefficients for each compound in this medium and because some of these were inconveniently low, they were calculated from the data at higher acidities by making the assumption that both positions in a given compound have the same rate–acidity profile. We believe this to be reasonable because hydrogen bonding reduces the electron density in the ring and this should affect the positional reactivities by comparable amounts since they are of fairly similar reactivity. (This will be confirmed in a subsequent paper on the reactivity of dithienobenzenes.) Any error in this assumption would make only a small error in the calculated overall reactivities of the β-positions, but *not* their relative reactivities (see Table 2).*

(iii) From the rate coefficients in 15% CF_3CO_2H–85% HOAc and the relative reactivity of [^{3}H]mesitylene

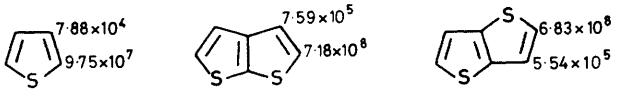


FIGURE 1 Partial rate factors for detritiation, free from hydrogen bonding

in 100% CF_3CO_2H and 15% CF_3CO_2H–85% HOAc (195 000), the rate coefficients for hydrogen exchange in 100% CF_3CO_2H in the absence of hydrogen bonding may be calculated and these values are up to 10-fold greater than the observed values (Table 2). From the calculated values, and the rate coefficient (0.095×10^{-7} s^{-1}) for detritiation of benzene under the same conditions,[24] the partial rate factors are obtained (Figure 1). These lead in turn to the corresponding σ^+-values (Figure 2), and the values for thiophen replace those given previously [25] which related to the hydrogen-bonded molecule.

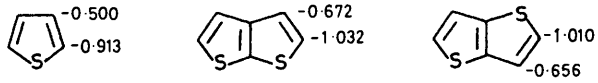


FIGURE 2 σ^+-Values

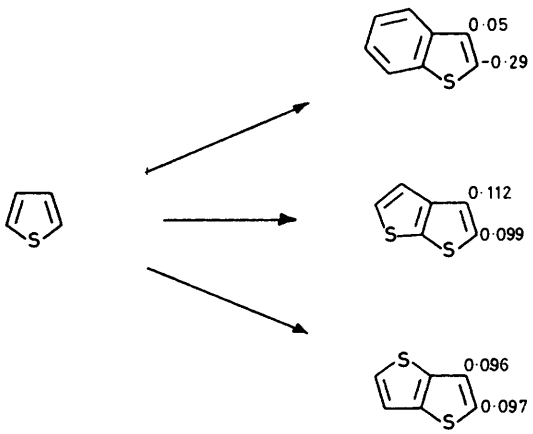
(iv) There is a good general agreement between our data and those given in Table 1. For example the approximate relative reactivities of the α-positions in dedeuteriation is confirmed in detritiation. Moreover the relative reactivity of 2-(I) : 2-thiophen in acetylation is 3.17 which corresponds to a σ^+ difference of *ca.* 0.06; likewise the ratio in chlorination corresponds to a σ^+ difference of 0.11, both values being close to the value of 0.10 from detritiation. The reactivity order 3-(I) >3-(II) holds under all conditions and indeed the reactivity ratios in detritiation and acetylation are identical. The discrepancy noted in the introduction *viz.* that the ratio 2-(I) : 2-(II) differs between acetylation and hydrogen exchange on one hand, and chlorination and formylation on the other, is confirmed. We believe that this is due to the greater polarisability of (II) than of (I), possibly deriving from the fact that there are five valence bond structures for α-substitution in (II), but only four for (I), though against this explanation must be set the fact that a greater proportion of the structures involved in the latter involve the polarisable π-electrons on sulphur. Thus in acetylation and hydrogen exchange (ρ = *ca.* −9 for each) the 2-(I) position is the more reactive. For chlorination however (ρ −10), the greater polarisability of (II) and the greater demand for resonance arising from the less reactive electrophile, now makes the 2-position of (II) the more reactive. The ρ-factor for formylation is not known, but the rate spreads in Table 1 show that it is greater than for chlorination; earlier work on formylation of five-membered heterocycles (*i.e.* containing a range of Group VI elements) showed that the ρ-factor must be substantially higher than in acetylation.[26] Hence in this reaction too, the 2-position of (II) is the more reactive. It would be interesting to have results for a reaction with an unselective (*i.e.* reactive) electrophile, and we predict for this a greater 2-(I) : 2-(II) ratio than found for acetylation and hydrogen exchange. The effect of this polarisability is of course to negate vigorous application of the Extended Selectivity Relationship, *i.e.* the derived σ^+-values do not predict the relative reactivities under all conditions.

(v) The relative reactivities are quite well predicted by calculations. The simple Hückel MO method using

* It might be argued that differential solvation effects account for these results. Thus for example the low reactivity of anisole in CF_3O_2H would then arise because its transition state is poorly solvated relative to its ground state, compared to alkylbenzenes. But anisole, being more polar should be better solvated, and steric hindrance to solvation is unimportant in CF_3CO_2H.[1] Moreover, its reactivity in CF_3CO_2H is precisely predicted by its σ^+-value in the presence of hydrogen bonding.[19] We therefore discount this possibility.

$h = 1.0$, $k = 0.6$ for sulphur [27] gives localization energies which predict the order: 2-thiophen >2-(II) > 2-(I) > 3-(I) > 3-(II) > 3-thiophen, the corresponding values of $\Delta E/ - \beta$ being 1.696, 1.698, 1.712, 1.774, 1.814, and 2.232; the only serious discrepancy is the high predicted reactivity of the 2-position of thiophen. A better result is provided by the CNDO/2 method which takes all valance electrons into account.[28] This predicts 2-(II) > 2-(I) > 2-thiophen > 3(I) > 3-(II) > 3-thiophen, and as our analysis shows, the order 2-(II) > 2-(I) should be obtained in high ρ-factor reactions, *i.e.* those with transition states closest to the Wheland intermediate. Localization energy calculations assume of course that the transition state is the Wheland intermediate.

(vi) Annelation of thiophen by benzene, and by thiophen, produces the change in σ^+-values shown in the Scheme. Notable is the fact that whereas benzene annelation changes the relative α : β-reactivities, annelation by thiophen (in either configuration) produces much the same effect at both positions. The former result



SCHEME Change in σ^+-values on annelation of thiophen

arises because both canonical forms of the resonance hybrid for β-substitution are benzenoid, whereas only one of those for α-substitution is benzenoid, *i.e.* the resonance energy of benzene plays an important role. The resonance energy of thiophen is by contrast substantially lower, so that its differential effect on the stabilities of the resonance hybrid for α- and β-substitution is smaller. An additional factor must be that two of the canonical forms for α-substitution of thienothiophens involve the sulphur π-electrons, *cf.* only one for benzo[*b*]thiophen. For β-substitution however there is only one structure involving the sulphur π-electrons in each case.

EXPERIMENTAL

[2-^{3}H]*Thieno*[2,3-b]*thiophen.*—*2,3,5-Tribromothiophen.* Thiophen was brominated according to the literature method [29] to give after normal work-up and fractional distillation, 2,3,5-tribromothiophen (72%), b.p. 80 °C at 0.5 mmHg (lit.,[23] 123—124 °C at 9 mmHg) and this crystallised on standing to a solid, m.p. 29—30 °C.

3-Bromothiophen. 2,3,5-Tribromothiophen was debrominated according to the literature method [30] to give 3-bromothiophen (64%), b.p. 159—162 °C (lit.,[30] 159—160 °C), n_D^{20} 1.5921 (lit.,[30] n_D^{20} 1.5919—1.5928).

3-Methylthiophen. 3-Bromothiophen (32.6 g, 0.2 mol) was added dropwise to a solution of n-butyl-lithium (168 ml of a 1.6N solution in hexane) in THF in a three-necked flask equipped with a stirrer, cooled to −78 °C, and swept with nitrogen. After 1 h, methyl iodide (32 g, 0.22 mol) was added and the mixture allowed to attain room temperature. Hydrolysis, normal work up, and fractional distillation gave 3-methylthiophen (18 g, 92%), b.p. 114—116 °C, n_D^{20} 1.5211 (lit.,[31] b.p. 115.4 °C, n_D^{20} 1.5204).

3-Bromomethylthiophen. Bromination of 3-methylthiophen according to the literature method [32] gave 3-bromomethylthiophen (56%), b.p. 75—80 °C at 2 mmHg, n_D^{20} 1.596 (lit.,[32] b.p. 75—80 °C at 1 mmHg, n_D^{20} 1.604). This product is unstable and rapidly darkens with evolution of hydrogen bromide.

Thiophen-3-carbaldehyde. This was prepared by two routes. The first (literature) [32] method using 3-bromomethylthiophen as starting material gave thiophen-3-carbaldehyde (28%), b.p. 58—60 °C at 4 mmHg, n_D^{20} 1.5855 (lit.,[32] b.p. 195—199 °C at 744 mmHg, n_D^{20} 1.5860).

The second, and better method, used 3-bromothiophen as the starting material. n-Butyl-lithium (68 ml of a 1.6N solution in hexane) was added to THF (110 ml) in a three-necked flask at −78 °C under nitrogen. A solution of 3-bromothiophen (32.6 g, 0.2 mol) in THF (30 ml) was added to the stirred solution. After 1 h, dry dimethylformamide (16.1 g, 0.22 mol) was added, the mixture allowed to attain room temperature, and then poured into cold dilute hydrochloric acid. Normal work up followed by fraction distillation gave thiophen-3-carbaldehyde (94%), b.p. 58—63 °C at 4.5 mmHg, n_D^{20} 1.5861.

Thiophen-3-carbaldehyde ethylene acetal. Thiophen-3-carbaldehyde was converted according to the literature method [33] into thiophen-3-carbaldehyde ethylene acetal (87%), b.p. 61—63 °C at 0.9 mmHg (lit.,[33] 103—104 °C at 10 mmHg), τ ($CDCl_3$) 2.91 (3 H, m, ArH), 4.18 (1 H, s,ArCH), and 6.20 [4 H, s, $(CH_2)_2$]. This was converted according to the literature method [34] into thieno[2,3-*b*]thiophencarboxylic acid (89%), m.p. 243.5—244 °C (lit.,[34] 242—244 °C), and this in turn to thieno[2,3-*b*]thiophen (80%), b.p. 61—62 °C at 2 mmHg (lit.,[34] 95 °C at 10 mmHg), τ ($CDCl_3$), 2.70 (2 H, m, ArH) and 2.92 (2 H, m, ArH).

Thieno[2,3-*b*]thiophen (1 g, 0.0093 mol) in THF (5 ml) was treated with n-butyl-lithium (*ca.* 1 ml of a 1.6N solution in hexane) at room temperature under nitrogen. After 10 min, the mixture was hydrolysed with tritiated water (180 μl; 100 mCi ml^{-1}) followed by dilute hydrochloric acid. Normal work-up and fractional distillation gave [2-^{3}H]-thieno[2,3-*b*]thiophen (70%), b.p. 94—96 °C at 10 mmHg, specific activity, 4 mCi g^{-1}.

[2,3,5,6-$^3H_4$]*Thieno*[2,3-b]*thiophen.*—A mixture of thieno-[2,3-*b*]thiophen (1 g, 0.0093 mol), trifluoroacetic acid (5 g, 0.0434 mol), and tritiated water was heated at 70 °C for 10 h in a sealed ampoule. This was then broken under sodium hydroxide solution and ether, extracted and worked up to give [2,3,5,6-$^3H_4$]thieno[2,3-*b*]thiophen (95%), specific activity 3.4 mCi g^{-1}.

[2-^{3}H]*Thieno*[3,2-b]*thiophen.*—*Thiophen-3-ylthioacetic acid.* A solution of 3-bromothiophen (32 g, 0.2 mol) in

THF (40 ml) was added to a stirred solution of n-butyllithium (137 ml of a 1.6N solution in hexane) at −78 °C under nitrogen. After 1 h sulphur (7 g, 0.2 mol) was added, stirring was continued during a further 4 h, and the mixture poured into a neutral solution of chloroacetic acid (18.6 g) and potassium carbonate (13.6 g) in water (250 ml). The mixture was stirred during 15 h and extracted with ether. The aqueous layer was acidified (giving a brown oil) which was extracted with ether and dried (Na_2SO_4). Ether was removed from the filtered solution, the residue taken up in the minimum of ether, cooled in ice, and then diluted with a very large excess of hexane, which precipitated thiophen-3-ylthioacetic acid (60%), m.p. 51—52 °C (lit.,[35] 51.5—52.5 °C), τ ($CDCl_3$) 2.88 (3 H, m, ArH) and 6.42 (2 H, s, CH_2).

Thiophen-2-ylthioacetic acid. This compound, m.p. 44—46 °C (lit.,[36] 42—46 °C), was prepared in 67% yield from thiophen according to the literature method,[36] τ ($CDCl_3$) 2.58, 2.73, and 3.00 (3 H, m, ArH) and 6.51 (2 H, s, CH_2).

2,3-*Dihydro*-3-*oxothieno*[3,2-b]*thiophen.* This compound, m.p. 98.5—99 °C (lit.,[37] 98—98.5 °C) was prepared in 10% yield from thiophen-3-ylthioacetic acid according to the literature method. A slightly less pure sample was also prepared in 9% yield by ring closure of thiophen-2-ylthioacetic acid (migration of the thioacetic acid group to the 3-position is a precursor to the ring closure [37]).

These products were reduced according to the literature [37] to give thieno[3,2-*b*]thiophen (69%), m.p. 55.5—58 °C (lit.,[37] 55.5—60 °C), τ ($CDCl_3$) 2.50 (2 H, m, ArH) and 2.69 (2 H, m, ArH). This was labelled in the 2-position as for the isomer above to give [2-^{3}H]thieno[3,2-*b*]thiophen (80%), m.p. 54—57 °C, specific activity, 9 mCi g^{-1}.

[3-^{3}H]*Thieno*[3,2-b]*thiophen.* Sodium borotritiide (12.5 mCi) suspended in absolute ethanol was added to a stirred solution of 2,3-dihydro-3-oxothieno[3,2-*b*]thiophen (1 g, 0.0064 mol) in absolute ethanol (5 ml). After 15 min a suspension of sodium borohydride (150 mg, 0.004 mol) in absolute ethanol (2 ml) was added, the temperature being maintained below 25 °C. After the mixture was heated to 50 °C during 1 h, the ethanol was removed by distillation, the residue hydrolysed with water (10 ml), and then made strongly acidic with 5N-hydrochloric acid. Normal work up followed by two recrystallisations from light petrolem (b.p. 80—120 °C) gave [3-^{3}H]thieno[3,2-*b*]thiophen (0.7 g, 78%), m.p. 52—55 °C, specific activity 4.1 mCi g^{-1}.

Kinetic Studies.—The general method has been described.[38] The acid media of concentrations common to those given in ref. 22 are from the same batch; the 75% CF_3CO_2H–25% HOAc (v/v) was prepared from AristaR acetic acid and purified CF_3CO_2H.[39] Kinetic runs on the double labelled compound gave curved kinetic plots and these were resolved into the two first-order components in the usual way. All runs were duplicated and the average rate coefficients are given in Table 2.

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