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THE RATES OF BASE CLEAVAGE OF SUBSTITUTED 2-THIENYLTRIMETHYLSILANES. AB INITIO CALCULATIONS OF THE ACIDITIES OF MONOSUBSTITUTED THIOPHENS *

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Summary

Rates of cleavage in NaOMe-MeOH at 50°C have been determined for the mono-substituted 2-trimethylsilylthiophens $X\cdot C_4H_2S\cdot SiMe_3$-2 with X = H, 3-$NO_2$, 3-Br, 4-Br-, and 5-$NO_2$, -CN, -COPh, -Me, -OMe and -NMe_2, and for one disubstituted compound, 4,5-$Br_2\cdot C_4HS\cdot SiMe_3$-2. For several compounds the rate and product isotope effects have also been determined. The energies involved in the process $X\cdot C_4H_3S \rightarrow X\cdot C_4H_2S^-$ for deprotonation at the 2-position have been calculated by an ab initio method (STO-3G), and the results used in analysis of the substituent effects in the cleavage of the $XC_4H_2S\cdot SiMe_3$-2 compounds. The results are consistent with the view the aryl anions separate in the rate-determining step of the cleavage. The isotope effects are all close to unity, whereas by comparison with results for $XC_6H_4CH_2SiMe_3$ and related species of similar reactivity, values in the region of 10 would be expected for the 3- and 5-NO_2 compounds if the product isotope effect for a carbanion R depended only in the pK_a of RH. The difference between the thienyl- and benzyl-type anions is attributed to the absence of conjugative delocalization of the charge in the former.

Approximate pK_a values are derived for the 2-positions of the $X\cdot C_4H_3S$ compounds.

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Introduction

We recently discussed the effects of the substituents X on the rate of cleavage of $XC_6H_4SiMe_3$ compounds by NaOH in H_2O-Me_2SO in the light of ab initio calculations of the energy required to deprotonate the corresponding XC_6H_5 species at the appropriate positions, and concluded that the effects were consistent with rate-determining separation of the anions $XC_6H_4^-$, without electrophilic assistance by proton transfer from the solvent to the separating carbon atom [1,2]. We have now determined the rates of cleavage of some thiophen derivatives, $X{\cdot}C_4H_2S{\cdot}SiMe_3$, in NaOMe-MeOH, a medium in which the possibility of electrophilic assistance can be investigated through examination of solvent isotope effects [1—8]. We have also carried out ab initio calculations of the energy required to remove a proton from the 2-position in various monosubstituted thiophens $X{\cdot}C_4H_2S$, and discuss the cleavage data in the light of the results.

Experimental

Preparation of 2-trimethylsilylthiophens

5-Nitro-2-trimethylsilylthiophen was made by nitration [9] of 2-trimethylsilylthiophen. The other 2-trimethylsilylthiophen compounds were mostly made from the appropriate 2-lithiothiophen compounds and Me_3SiCl in ether, but in some cases the 2-sodio derivatives were used. After a period of refluxing the cooled mixture was treated with cold saturated aqueous ammonium chloride, and the ethereal layer was washed, dried (Na_2SO_4) and fractionated. Approximate boiling points, NMR data, and analyses are listed in Table 1.

Details are as follows.

TABLE 1

BOILING POINTS, ANALYSES AND ^{1}H NMR SPECTRA FOR RING-SUBSTITUTED 2-TRIMETHYLSILYLTHIOPENS

Substituent(s)	b.p. (°C/ mmHg)	Analyses found(calcd.) (%)		^{1}H NMR spectra (δ, ppm) [a]
		C	H	
5-NMe_2	87/2	53.9(54.2)	8.6(8.6)	0.23(s, 9 H); 2.87(s, 6 H); 5.8(d, 1 H); 6.71(d, 1 H)
5-OMe	115/38	51.4(51.6)	7.7(7.6)	0.27(s, 9 H); 3.80(s, 3 H); 6.11(d, 1 H); 6.7(d, 1 H)
5-Me	98/35	56.4(56.4)	8.1(8.3)	0.27(s, 9 H); 2.48(s, 3 H); 6.66(m, 1 H); 6.88(d, 1 H)
5-H	168/760			
5-Cl	100/40	44.2(44.1)	5.5(5.8)	0.30(s, 9 H); 6.83(d, 1 H); 6.90(s, 1 H)
5-Br	118/38 [b]			0.30(s, 9 H); 6.87(d, 1 H); 6.93(d, 1 H)
4-Br	126/30	35.9(35.7)	4.9(4.7)	0.30(s, 9 H); 7.03(d, 1 H); 7.33(d, H)
3-Br	110/22	35.7(35.7)	4.8(4.7)	0.40(s, 9 H); 7.03(d, 1 H); 7.4(d, 1 H)
4,5-Br_2	155/20	26.3(26.8)	3.2(3.2)	0.30(s, 9 H); 6.93(s, 1 H)
5-COPh	170/1	65.1(64.6)	6.3(6.2)	0.37(s, 9 H); 7.17(d, 1 H); 7.36—7.9(m, 6 H)
5-CN	120/10	52.5(53.0)	6.1(6.1)	0.40(s, 9 H); 7.17(d, 1 H); 7.57(d, 1 H)
3-NO_2	120/10	41.7(41.8)	5.5(5.5)	0.43(s, 9 H); 7.43(d, 1 H); 7.72(d, 1 H)
5-NO_2	150/20	41.3(41.8)	5.6(5.5)	0.37(s, 9 H); 7.07(d, 1 H); 7.80(d, 1 H);

[a] In CCl_4 with Me_4Si as internal standard. [b] Lit., b.p. 218—218.5°C/760 mm [33].

(a) Thiophen, and 2-methoxy- and 2-methyl-thiophen were lithiated with n-BuLi in Et_2O at 0° C; after addition of Me_3SiCl the mixture was refluxed for 4 h then worked up [10].

(b) 2,3-Dibromothiophen was lithiated with n-BuLi in Et_2O at —70°C. After addition of Me_3SiCl the mixture was refluxed for 1 h. The 2-bromotrimethylsilylthiophen obtained from the initial fractionation contained a little 2,3-bis(trimethylsilyl)thiophen, which was removed by careful refractionation.

(c) 2,3-Dibromothiophen was treated with $LiN(Pr\text{-}i)_2$ at —70° C; after 1 h Me_3SiCl was added, and the mixture was kept at room temperature for 12 h. The usual work-up gave 4,5-dibromo-2-trimethylsilylthiophen. The product contained ca. 15% of isomers which could not be removed, but these are thought not to affect the kinetic results significantly.

(d) 4,5-Dibromo-2-trimethylsilylthiophen was treated with n-BuLi in Et_2O at —70° C for 0.5 h, and moist ether then water were added to the mixture at this temperature. The usual work-up gave 4-bromo-2-trimethylsilylthiophen. This contained ca. 15% of an isomeric impurity but this is thought not to affect the kinetic results significantly.

(e) 3-Nitro- and 2-cyano-thiophen were treated for 0.5 h in Et_2O at —78° C with lithium diisopropylamide-HMPT [11], then Me_3SiCl was added during 0.5 h. The mixture was set aside at room temperature for 18 h then worked up as usual, but with several washings of the ethereal layer to remove any HMPT.

5-Dimethylamino-2-trimethylsilylthiophene was prepared analogously, but with THF in place of ether as solvent.

(f) 2-Chloro- and 2-bromo-thiophen were treated with sodium shot in Et_2O [12] to give the 5-halogeno-2-sodiothiophen, and Me_3SiCl was added. The mixture was refluxed for 18 h then worked up as usual.

(g) 2-Trimethylsilylthiophen was treated with n-BuLi in Et_2O and the mixture was refluxed for 4 h. Benzonitrile in Et_2O was added at 0° C, and the mixture was kept overnight at room temperature then treated with saturated aqueous NH_4Cl at 0° C. The ethereal layer was refluxed gently for 2 h with 5% hydrochloric acid to give the 5-benzoyl-2-trimethylsilylthiophen [13].

Rate measurements

Rates were measured spectrometrically by the usual procedures [3] at the wave-lengths listed in Table 2. The reaction mixtures were usually contained in thermostated cells, but for the slow runs (for $5\text{-X}\cdot C_4H_2S\cdot SiMe_3\text{-}2$ with X = H, Me, OMe, and NMe_2) sealed ampoules were used [3].

In the case of $5\text{-NC}\cdot C_4H_2S\cdot SiMe_3$ some conversion of cyano- into imidate groups occurs in both reactant and cleavage product ($2\text{-NC}\cdot C_4H_2S$). (This complication has been discussed for *m*- and *p*-$NCC_6H_4CH_2SiMe_3$ [8].) This reaction is slow compared with the cleavage, and probably less than 15% of the imidate would be present even at equilibrium, but it does mean that the infinity value of the absorbance cannot be obtained directly, and the Swinbourne method [14] was used to determine the rate constant, which is subject to an estimated uncertainty of ±10%.

The results, with the exception of those for the $2\text{-}Me_2N$- derivative, are shown in Table 2, which gives the value of the second order specific rate constants, k_s, (the observed first order rate constant divided by the NaOMe

TABLE 2

RATES AND ISOTOPE EFFECTS IN CLEAVAGE OF SUBSTITUTED 2-TRIMETHYLSILYLTHIOPHENS BY NaOMe—MeOH AT 50.0°C

Substituents	λ (nm)	[NaOMe] (*M*)	$10^5 k_s$(MeOH) (l mol^{-1} s^{-1})	$10^5 k_s$(MeOD) (l mol^{-1} s^{-1})	k_{rel} [a]	RIE	PIE [b]
3-NO_2	310	0.001	1 050 000	2 120 000	1.75×10^6	0.50	1.2 [c]
5-NO_2	330	0.001	520 000	1 230 000	8.75×10^5	0.42	1.1 [d]
5-CN	281	0.005	77 000	170 000	1.29×10^5	0.45	
5-COPh	320	0.2	3 000	6 900	5.0×10^3	0.43	1.1
3-Br	260	1.0	1 100	2 300	1.46×10^3	0.48	
4-Br	260	1.0	210	440	2.84×10^2	0.48	
	260	0.2	170				
5-Br	260	1.0	97	220	1.30×10^2	0.45	1.2
	260	0.2	78				
4,5-Br_2	260	0.1	11 700		1.56×10^4		
5-Cl	260	1.0	71	150	9.5×10	0.47	1.2
None	245	1.0	0.75		1.0		1.0
5-Me	250	1.0	0.15		0.20		
5-OMe	260	1.0	0.45	0.90	0.60	0.50	
5-NMe_2					0.04 [e]		

[a] Corrected where appropriate for the dependence of k_s on [NaOMe]. [b] Determined by use of MPD analyzer (see Experimental section) unless otherwise indicated. [c] By NMR method. [d] Value of 1.2 obtained by NMR method. [e] See Table 3 and Discussion.

concentration); the base concentration used in each case is approximately indicated since at higher concentrations k_s varies with [NaOMe], as previously noted [7] and as can be seen from the data for the 4- and 5-bromo compounds. Values of k_s observed at 1 *M* NaOMe should be multiplied by 0.8 to be directly comparable with those at the lower base concentrations; this correction has been made in the values of the relative rate constants k_{rel} (k_s for the compound concerned divided by that for 2-$Me_3Si \cdot C_4H_2S$) shown in Table 2.

Also shown in Table 2 are the values of the rate isotope effect, RIE, given by the ratio of the k_s value in MeOH to that in MeOD at similar base concentrations.

Results for 2-$Me_2N \cdot C_4H_2S \cdot SiMe_3$ are listed in Table 3.

Product isotope effects

The product ratios RH/RD obtained on cleavage in 1 : 1 MeOH-MeOD were

TABLE 3

OBSERVED FIRST ORDER RATE CONSTANTS FOR CLEAVAGE OF 5-$Me_2N \cdot C_4H_2S \cdot SiMe_3$ AT VARIOUS CONCENTRATIONS OF NaOMe IN MeOH AT 50.0°C [a]

[NaOMe] (*M*)	$10^5 k$(s^{-1})
0.00	17
0.001	2.7
0.01	0.77
0.10	0.45
1.00	0.275
2.00	0.325

[a] A wave-length of 300nm was used to monitor the cleavage.

TABLE 4

DEPROTONATION ENERGIES, $E_X - E_{X^-}$, GIVEN BY THE DIFFERENCE IN ENERGY BETWEEN THE NEUTRAL X·C_4H_3S SPECIES AND THE X-THIEN-2-YL ANIONS

No.	X	$10^4(E_X - E_{X^-})$ (a.u.) [b]	$10^3 \times \Delta E_{X^-}$(a.u.)	$10^3 \times \Delta E_{X^-}(XC_6H_4^-)$ [b] (a.u.)
1	5-NO_2	7612	49	42
2	5-F	8028	7	7
3	3-Cl	7804	30	29
4	4-Cl	7858	24	23
5	5-Cl	7859	24	20
6	H	8102	0	0
7	5-Me	8121	−2	−2
8	5-OMe	8089	1	−2
9	5-NH_2 [c]	8146 [c]	−4 [c]	−7 [c]
	(5-NH_2) [d]	(8206) [d]	(−10) [d]	(−14) [d]

[a] Other substituents used in the plots are numbered as follows: 3-Br, 10; 4-Br, 12; 5-Br, 12; 5-CN, 13; 5-COPh, 14; [b] Deprotonation energies for 1-position of XC_6H_5, with *o*-, *m*-, and *p*-X taken as corresponding to 3-, 4-, and 5-X in the thiophen series. [c] Optimized geometry at nitrogen. [d] Planar geometry at nitrogen.

determined as previously described either by use of an Applied Chromatography Systems Organic Analyzer MPD 850 linked to a Pye Model 64 gas chromatograph [3] or by an NMR method using the signal from the 2-H [6]. For the one case, 5-O_2N·C_4H_2S·$SiMe_3$, in which both methods were used the two methods were in good agreement (Table 2).

TABLE 5

10^3 CHARGES (*e*) AT VARIOUS POSITIONS OF THIOPHEN AND 5-NITROTHIOPHEN AND THE ANIONS DERIVED FROM THEM BY DEPROTONATION AT THE 2-POSITION

Posn.	Thiophen			Thien-2-yl anion		
	σ	π	total	σ	π	total
S	9	253	263	−160	203	43
2-C	−103	−76	−179	−710	346	−364
3-C	−50	−36	−86	69	−312	−244
4-C	−50	−36	−86	−88	−24	−111
5-C	−103	−76	−179	−46	−213	−259
2-H	70		70			
3-H	64		64	−37		−37
4-H	64		64	−12		−12
5-H	70		70	−17		−17
Posn.	5-Nitrothiophen			5-Nitrothien-2-yl anion		
	σ	π	total	σ	π	total
S	60	265	325	−89	211	122
2-C	−126	−34	−161	−725	405	−320
3-C	−22	−59	−81	59	−281	−221
4-C	−73	24	−49	−129	63	−66
5-C	111	−157	−45	148	−274	−126
2-H	89		89			
3-H	79		79	−11		−11
4-H	98		98	33		33
N	379		−233	335	−198	136
O_2	−595	195	−400	−620	74	−545

TABLE 6

CHARGES AT 2-H IN THE MONO-SUBSTITUTED THIOPHENS $X\text{-}C_4H_3S$

X	$10^3 C$ (e)	$10^3\ \Delta C$ (e) [a]	X	$10^3 C$ (e)	$10^3\ \Delta C$ (e)
5-NO_2	89	19	H	70	0
5-F	74	4	5-Me	68	−2
4-Cl	80	10	5-OMe	68	−2
5-Cl	79	9	5-NH_2	66	−4

[a] $\Delta C = C$ for X = X minus C for X = H.

Calculations

Minimum basis set (STO-3G) ab initio calculations were carried out using the Gaussian 70 package [15]. Standard geometries [16] were used for the substituents in association with the experimental geometry for thiophen [30], except for the 2-amino-compound, for which the geometry at the nitrogen in the neutral species and the anion were optimized as in ref. 2; the HNH angles thus derived were 111.5 and 108.4°, respectively. (Values of 112.1 and 108.5° were calculated for aniline and the $p\text{-}H_2NC_6H_4^-$ anion [2].) The S *d*-orbitals were not included.

The values of the deprotonation energies, $E_X - E_X^-$, given by the difference in energy between the neutral and the anionic species are shown in Table 4 along with the value ΔE_X^- of the deprotonation energy relative to that for X = H. Values of ΔE_X^- for corresponding XC_6H_5 species are also shown for comparison.

The charge distributions for thiophen, the thien-2-yl, and the 5-nitrothien-2-yl anion are shown in Table 5, and calculated charge densities on the hydrogen atom at the 2-position in various $X\cdot C_4H_3S$ species are listed in Table 6. Charge distributions for some mono-substituted thiophens were reported earlier by Kao and Radom [17].

Results and discussions

Charge distribution and deprotonation energies

As Table 5 shows, a large proportion of the unit negative charge placed on the ring by deprotonation at the 2-position of thiophen is dispersed away from that position; the 2-position in the anion carries a negative charge of −0.364 *e*, but there is a total negative charge of −0.109 *e* on the 2-carbon plus its attached hydrogen atom in thiophen itself, and so only an additional 0.25 *e* remains at the 2-position, i.e. 25% of the additional charge in the anion. Some 22% of the additional charge is taken by the sulphur atom, 26% by the three remaining hydrogen atoms, and 26% by the other ring carbon atoms. A large proportion of the dispersal of the additional charge occurs by distortion of the π-system, additional π-charge of 0.276 and 0.137 *e* appearing on the 3- and 5-carbon atoms, respectively, with the σ-system then adjusting to accommodate the π-charges, as noted for the phenyl anion [2]. A significant amount of additional negative σ-charge, viz. 0.169 *e*, is taken by the sulphur atom, however, and this is accompanied by a decrease of 0.050 *e* in the positive π-charge there. In the 5-nitrothien-2-yl anion only 14% of the additional unit negative charge remains at the 2-position, some 15% being accomodated by the NO_2 group.

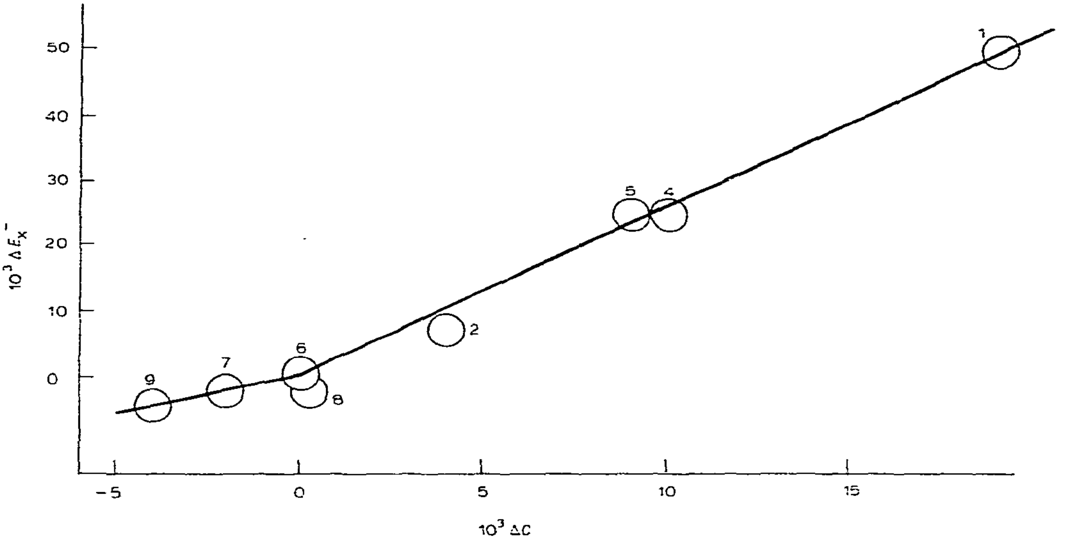

Fig. 1. Plot of ΔE_X^- (relative energies of deprotonation at the 2-position) against ΔC (relative charge at 2-H) for X-C_4H_3S species. The numbering of points is as in Table 4.

A plot of ΔC, the difference between the calculated charge on the 2-H atom of X·$C_4H_2S^-$ and that on the 2-H atom in C_4H_4S against the relative deprotonation energy ΔE_X^- gives a two line plot, as Figure 1 shows, one line for the origin and the electron-withdrawing substituents and the other for the origin and the electron-releasing groups Me, OMe, and NH_2; a similar plot was observed for the XC_6H_4 series [2,31], and, indeed, a plot of values of ΔC for the thiophen against those for the benzene series (4- and 5-X being regarded as equivalent to *m*- and *p*-X groups) is a good line (Figure 2) except for the seriously deviant point for X = F. As for the benzene series, we suggest that the two-line plot of Figure 2 is associated with the fact that the effects of electron-withdrawing groups on the anions parallel those on the initial X·C_6H_3S compounds, while the electron-release by Me, OMe, and NH_2 groups is inhibited in the anion compared with that in the neutral species.

We next compare the relative deprotonation energies ΔE_X^- for the substituted thiophens X·C_4H_3S with those for substituted benzenes, XC_6H_5, 3-, 4- and 5-X groups in the thiophens being regarded as equivalent to *o*-, *m*-, and *p*-groups, respectively, in the benzene series. Figure 3 shows that there is a satisfactory linear correlation between the two sets (corrln. coeff., 0.995; slope 1.07; intercept 1.58; 9 points), and an even better plot is obtained if only 5- and *p*-X groups are considered (corrln. coeff., 0.998; slope, 1.12; intercept, 1.87; 7 points). The best least squares line through all the points misses the origin by 1.6 units in $10^3\ \Delta E_X^-$ for the thiophens, and examination of the two sets of ΔE_X^- values in Table 3 shows that while the stabilizing effects of electron-withdrawing substituents are slightly larger for the thiophen than for the benzene series, the destabilizing effects of the electron-releasing substituents are smaller for the former than for the latter series. (Indeed, according to the calculations the 5-OMe group should slightly increase the ease of deprotonation,

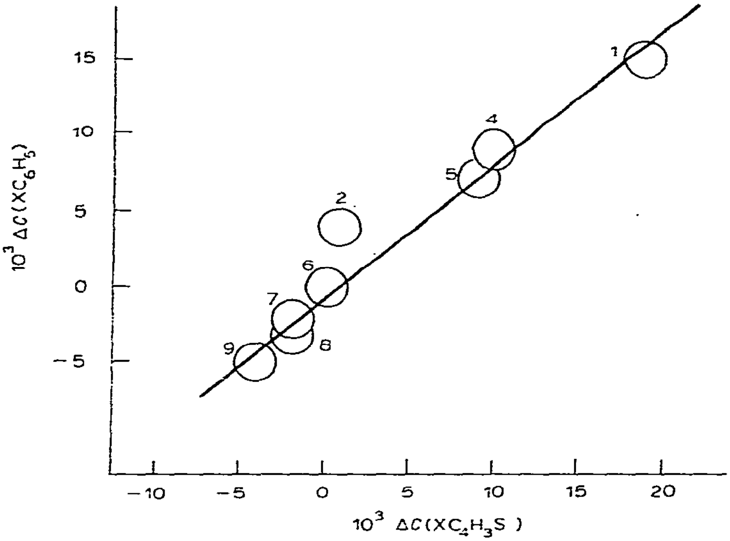

Fig. 2. Plot of ΔC (relative charge at 1-H) for XC_6H_5 against ΔC (relative charge at 2-H) for $X{\cdot}C_4H_3S$, with 4- and 5-X taken as corresponding to *m*- and *p*-X, respectively. The numbering of substituents is as in Table 4. The line shown is for the best least squares correlation with omission of the point for F (No. 2).

but the effect is certainly not outside the uncertainty in the calculations.)

A plot of the ΔE_X^- values for the thiophens against the σ^0 constants [19] for the benzene derivatives (with 4- and 5-X groups being regarded as equivalent to

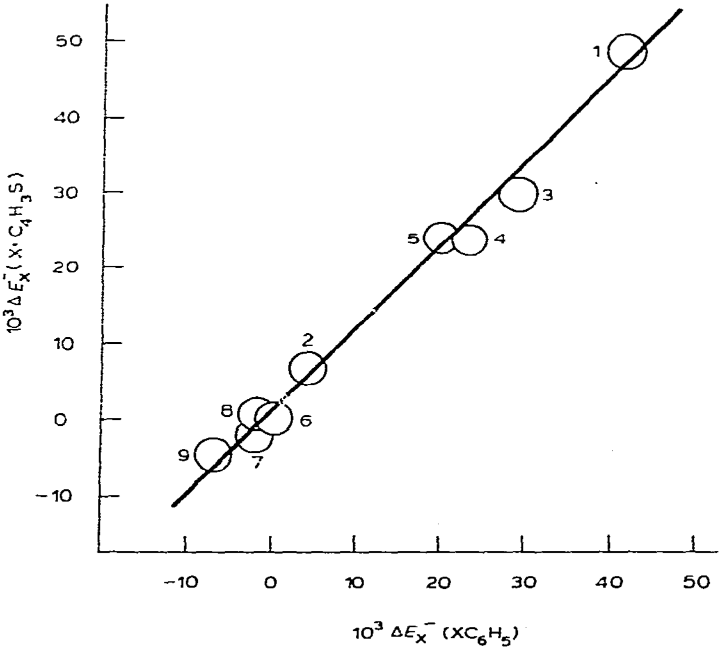

Fig. 3. Plot of ΔE_X^- for $X{\cdot}C_4H_3S$ against ΔE_X^- for XC_6H_5, with 3-, 4- and 5-X, taken as corresponding to *o*-, *m*-, and *p*-X. The numbering of substituents is as in Table 4.

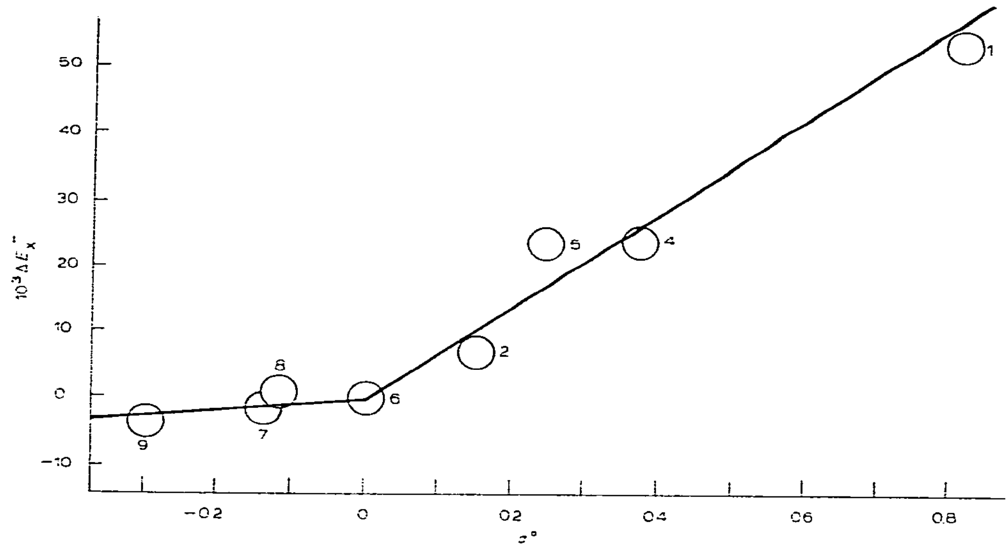

Fig. 4. Plot of ΔE_X^- for the substituted thiophens against σ^0 constants for benzene derivatives, with 4- and 5-X groups in thiophens being regarded as equivalent to *m*- and *p*-X groups in benzenes. The numbering of the groups is as in Table 4.

m- and *p*-X groups, respectively) is revealing in this connection; as Figure 4 shows, the plot is best regarded as two separate lines, one for the points for the electron-withdrawing groups and the origin, and the other, of much smaller slope, for the origin and the points for X = OMe, Me, and NMe_2 (NH_2). Such a plot is consistent with very substantial inhibition of the electron-releasing resonance effects of the latter of group. A similar two-line plot was observed for XC_6H_5 compounds, but with a much smaller disparity between the slopes of the lines [2]. It is thus likely that the inhibition of these electron-releasing effects is greater in the thienyl than in the phenyl anions, but since all the points in the plot of Figure 3 can be regarded as lying on the line when account is taken of the uncertainties in the calculations, there is no firm evidence for such a distinction between the two series.

Substituent effects and mechanisms

Only an approximate value of k_{rel} was obtained for the base-catalysed cleavage of $5\text{-}Me_2N{\cdot}C_4H_2S{\cdot}SiMe_3$ because there is interference from cleavage by other mechanisms, as can be deduced from the data in Table 3. There is a fairly rapid cleavage in methanol alone, and the presence of 0.001 *M* base causes a 5-fold fall in rate. The observed rate constant falls further with increasing concentration of base up to 1 *M*, but there is then a small increase on going to 2 *M* base. There is clearly an acid-catalysed process which contributes significantly even when 0.01 *M* base is present, and there seems also to be a neutral, "spontaneous" process which maintains the rate in the 0.01—1 *M* region. While the limited data available cannot be quantitatively interpreted in terms of concurrent acid-catalysed, spontaneous, and base-catalysed processes (we hope to carry out a more detailed study), the increase in the rate constant by 0.05 ×

10^{-5} s^{-1} on going from 1 *M* to 2 *M* base can reasonably be assumed to arise very substantially from the base catalysed process. After allowance for the variation of k_s with base-concentration in the range concerned [7], this corresponds to a k_s value of ca. 0.03 × 10^{-5} l mol^{-1} s^{-1} at a low base concentration, and thus a k_{rel} value of 0.04. The approximate value is used in the discussion below, and we note that even if the value were in error by a factor of 2, which is unlikely, the conclusions would not be significantly affected.

It will be seen from Table 2 that the substituted 2-thienyltrimethylsilanes show a very large range of reactivities; the 3-nitro group increases the rate more than 10^6 times. For the one di-substituted compound examined, 4,5-Br_2·C_4HS·$SiMe_3$, the combined effects of the two substituents are only slightly less than expected for exact additivity.

The correlation shown in Figure 3 suggests that if the cleavage of thienyl- and phenyl-trimethylsilanes both involve rate-determining separation of the aryl anions, then log k_{rel} values for the 5-X·C_4H_2S·$SiMe_3$ series would be expected to correlate linearly with those for the *p*-$XC_6H_4SiMe_3$ series, and Figure 5 shows that this is the case (corrln. coeff., 0.989; slope, 1.30; intercept, —0.27; 7 points). However, the best least squares line lies above the origin by 0.27 units, and examination of the two sets of k_{rel} values shows that while electron withdrawing groups activate more strongly in the thiophen than in the benzene series, the electron releasing groups MeO and NMe_2 deactivate less in the former than in the latter series. This is in keeping with the pattern of $\Delta E_X{}^-$

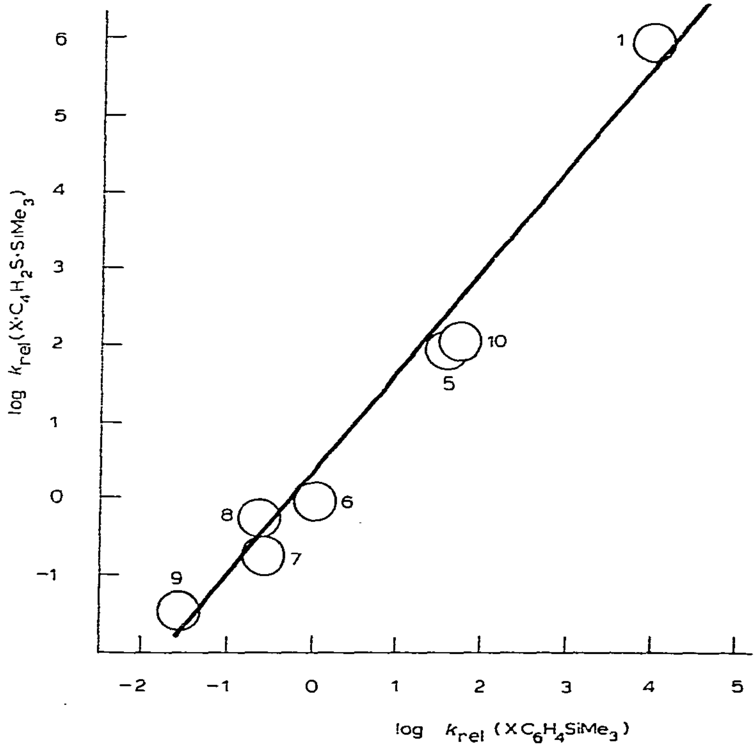

Fig. 5. Plot of log k_{rel} for cleavage of 5-X-C_4H_2S-$SiMe_3$-2 compounds in NaOMe-MeOH against log k_{rel} for cleavage of *p*-X-C_6H_4-$SiMe_3$ compounds in NaOH-H_2O-Me_2SO; the numbering is as in Table 4.

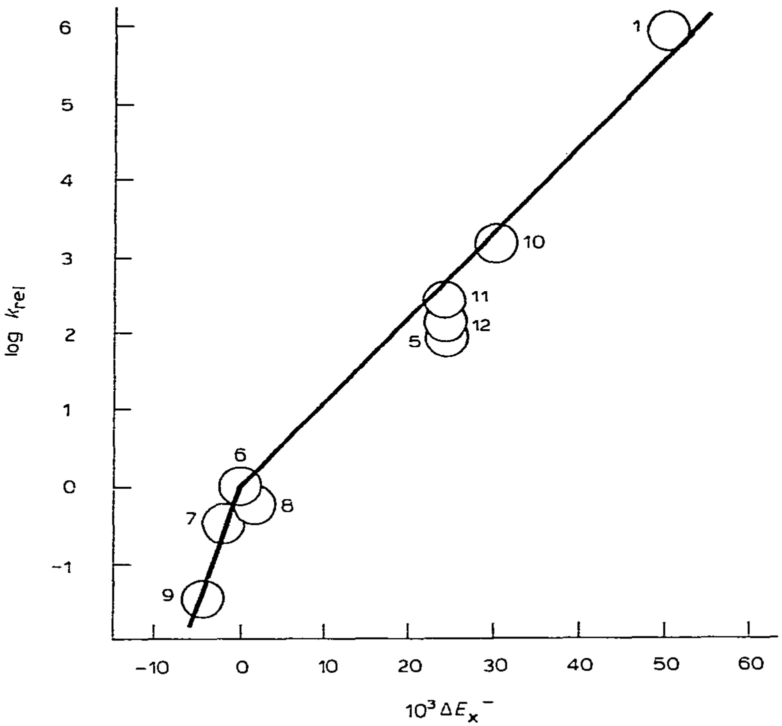

Fig. 6. Plot of log k_{rel} for cleavage of $X{\cdot}C_4H_2S{\cdot}SiMe_3$-2 compounds in NaOMe-MeOH against ΔE_X^- values. Numbering of substituents is as in Table 4; rate data for bromo-compounds are used in association with ΔE_X^- for chloro-compounds, and those for the 5-NMe_2 compound in association with ΔE_X^- for the 5-NH_2 compound.

values in the two series, and, like Figure 3, Figure 5 would possibly be better shown as two lines through the origin, one for electron-withdrawing and one for electron-releasing substituents.

It follows that a plot of log k_{rel} values for the $X{\cdot}C_4H_2S{\cdot}SiMe_3$ compounds against the ΔE_X^- values for $X{\cdot}C_4H_3S$ must resemble the corresponding plot for the $XC_6H_4SiMe_3$ compounds, and consist of two straight lines meeting at the origin, one through the points for electron-withdrawing groups and the other through the points for the electron-releasing groups *p*-OMe, *p*-Me, and *p*-NMe_2, and Figure 6 confirms that this is so *. We offer an explanation similar to that we proposed for the $XC_6H_4SiMe_3$ series [2], viz. that there is substantial inhibition in the anion $X{\cdot}C_4H_2S^-$ of the electron release by the *p*-Me, *p*-OMe, and *p*-NMe_2 groups, especially by the last, which is not reflected im the cleavage rates because the transition state is substantially removed from the anion; another aspect of this effect is touched on in the next paragraph.

As expected from the nature of the plots considered above, a plot of log k_{rel} for the $X{\cdot}C_4H_2S{\cdot}SiMe_3$-2 compounds against values [19] of δ_m^0 (for 4-X) or

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* Values of ΔE_X^- for Cl substituents have been used in association with log k_{rel} values for Br substituents, and, as previously [2], the ΔE_X^- value for the NH_2 group with the log k_{rel} value for the Me_2N group. Comparison of the σ^0 constants of the groups concerned justifies this approximation.

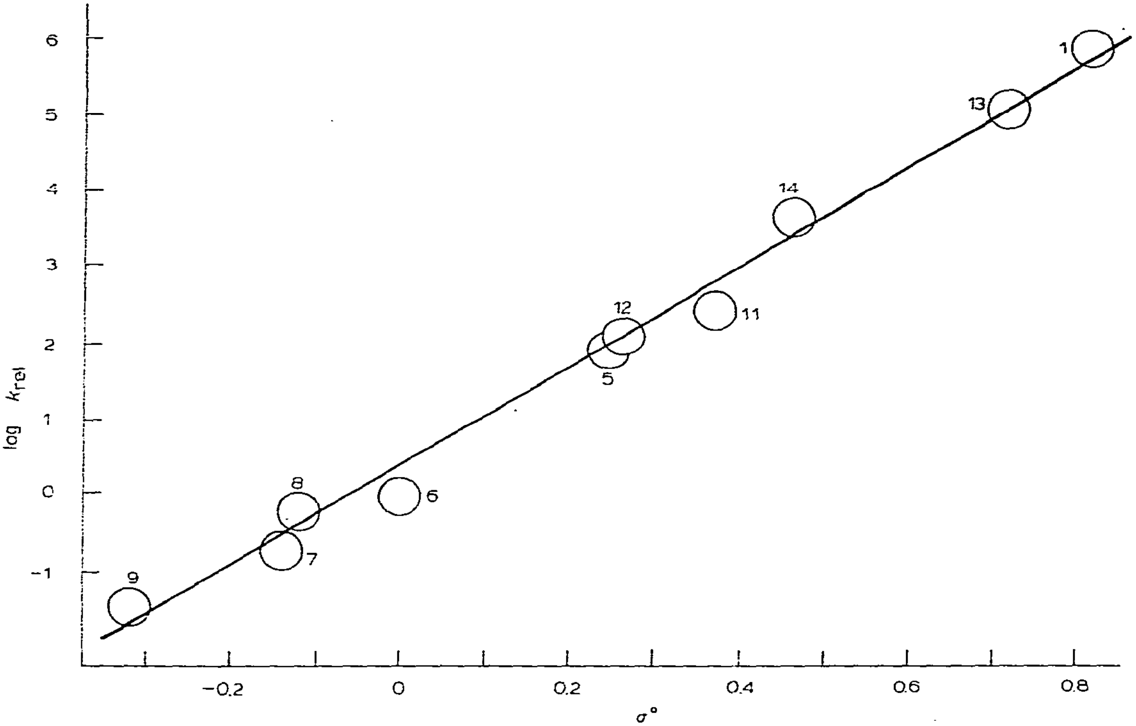

Fig.7. Plot of log k_{rel} for X-C_4H_2S-$SiMe_3$-2 compounds against σ^0 constants for benzene derivatives. with 4- and 5-X taken as equivalent to *m*- and *p*-X. The numbering is as in Table 4.

σ_p^0 (for 5-X) is a fairly good straight line (Figure 7; corrln. coeff. 0.995; slope 6.64; intercept 0.39; 10 points); the large value of the slope ρ is noteworthy. [If the points for OMe and NHe_2 are omitted, a line of slope 7.06 passing closer to the origin (intercept 0.18) is obtained.] As with cleavages of $XC_6H_4SiMe_3$ compounds, we think that σ^0 constants apply approximately to groups with electron-releasing effects only because the transition state is well-removed from the carbanion; for the deprotonation equilibrium X·C_4H_3S $\rightleftharpoons$ X·$C_4H_2S^-$ we could expect an approximate correlation with $[\sigma^0 + r(\sigma^+ - \sigma^0)]$ where r has a small negative value, the quantity $r(\sigma^+ - \sigma^0)$ reflecting the degree of suppression of resonance electron-releasing effects in the anion [2].

We should note that discussion above implies that for X·C_4H_2S·$SiMe_3$-2 and $XC_6H_4SiMe_3$ compounds containing groups such as OMe and NMe_2 which release electrons strongly by resonance effects, the normally observed relationship between the log k_s value for cleavage of $RSiMe_3$ and the pK_a of RH [20] will not apply, since the effects of the substituents on the transition state do not adequately reflect those on the carbanion R^-. For cleavage of $XC_6H_4CH_2SiMe_3$ compounds, in contrast, the substituent effects do reflect those on the carbanion, since σ^- constants apply [6,21]. It may be that in the thiophen and benzenes series, where the negative charge in the carbanion cannot be conjugatively delocalized, the suppression of the π-electron release by OMe and NMe_2 rises sharply only after a substantial proportion of the unit negative charge, say 60—70%, has developed at the carbanionic centre, whereas for generation of carbanions in which conjugative delocalization is possible there is a smooth progression in the substituent effects from the reactant to the carbanion.

Solvent isotope effects

Values of the rate (RIE) and product (PIE) isotope effects are shown for some of the compounds in Table 2. The RIE values fall in the range 0.43—0.50, consistent with rate-determining separation of the carbanion. A very interesting feature of the results is that the values of the product isotope effect, PIE (given by the product raio RH/RD formed on cleavage of $RSiMe_3$ in 1/1 MeOH-MeOD) for the $X{\cdot}C_4H_2S{\cdot}SiMe_3$ compounds examined are all close to unity. On the usual interpretation of kinetic effects [22], the PIE for the anion R^-, is expected to depend on the pK_a of the corresponding acid RH, and more specifically, for reactions in methanol, on the difference between the pK_a of RH and that of methanol; such a dependence was demonstrated for base cleavage of a series substituted benzylsilanes, $XC_6H_4CH_2SiMe_3$ and related species such as 9-fluorenyltrimethylsilane [4]. Furthermore, since the ease of cleavage of the $RSiMe_3$ compound should (in the absence of electrophilic assistance) normally parallel that of the acidity of RH, and appears to do so for a range of R species [20] *, $RSiMe_3$ compounds which are cleaved at similar rates should give roughly similar PIE's [4]. We showed more recently that the generalization did not apply with precision, since the picolyl and quinolylmethyl derivatives 4-$Me_3SiCH_2{\cdot}C_5H_4N$, 2-$Me_3SiCH_2{\cdot}C_9H_6N$, and 4-$Me_3SiCH_2{\cdot}C_9H_6N$ gave PIE's which, while sizeable (2.6 –5), were significantly lower than those for $XC_6H_4CH_2SiMe_3$ compounds of comparable reactivity, and we concluded that the parallel between k_s and PIE values for $RSiMe_3$ compounds cannot be carried over quantitatively from one type of R group to another [6], but it evidently breaks down completely on going to the thiophen series. The specific rate constants for the cleavage of the $X{\cdot}C_4H_2S{\cdot}SiMe_3$-2 compounds containing activating substituents span the range observed for the $XC_6H_4CH_2SiMe_3$ compounds, and the most reactive thienyl compound, 3-$O_2N{\cdot}C_4H_2S{\cdot}SiMe_3$-2 is some 220 and 45 times as reactive as *o*- and *p*-$O_2NC_6H_4CH_2SiMe_3$, respectively, and the latter both give PIE's of ca. 10, whereas the thienyl compound gives a value close to 1. The same anomaly arises, of course, if we try to relate the PIE's to the pK_a's for the corresponding RH acids. Thus from our $\Delta E_X{}^-$ values for the $X{\cdot}C_4H_3S$ compounds we derive approximate pK_a's of 15.5, 16.5, and 28.5 respectively, for X = 3-NO_2, 5-NO_2, and 5-COPh (see below), while the pK_a's for fluorene (9-position) [26], indene (1-position) [27] and *p*-nitrotoluene (α-position) are 22, 19.9, and ca. 21.5 **, respectively, and yet the PIE's for the thienyltrimethylsilanes are all near to 1, whereas those for 9-fluorenyl-, 1-indenyl-, and *p*-nitrobenzyl-trimethylsilane are in the region of 10 [4].

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* In the light of the discussion in this paper, it would not be surprising if the linear relationship between log k_s for $RSiMe_3$ and the pK_a of RH, established mainly for R groups giving delocalized carbanions, applied less satisfactorily to H groups giving non-delocalized carbanions, but in fact, the k_s values for H = PhC≡C, thien-2-yl, and benzothien-2-yl seem reasonably consistent with the relevant pK_a values [3,20].

** Estimated from value of 20.4 reported for solutions in Me_2SO [29], in which the pK_a of toluene is ca. 42. It is noteworthy that a pK_a of 21.5 places the point for *p*-$O_2NC_6H_4CH_2SiMe_3$ satisfactorily close to the log k_s-pK_a plot [20].

It is highly likely that the anomaly is to be associated with the fact that in the benzyl and related compounds the charge in the carbanion is extensively delocalized by conjugative effects, whereas in the thienyl carbanions no such delocalization is possible *. In other words, the distinction between the magnitudes of the PIE values in the two cases reflects, as it would be expected to, the distinction between the rates of protonation of delocalized and non-delocalized carbanions derived from acids of comparable equilibrium acidities as indicated by the pK_a's; for example, the rate of proton transfer to the anion $[CH_2NO_2]^-$, which is extensively delocalized, is much lower than would be expected from the pK_a of nitromethane [23,24]. The operation of the inverse effect can be seen in the fact that the proton transfer to the anion $PhC{\equiv}C^-$ (or from the acid $PhC{\equiv}CH$), in which no conjugative delocalization is possible, is much larger than those for carbanions derived from most other carbon acids of similar equilibrium acidity [24]. Hine explains the energy barrier for protonation of delocalized carbanions (or deprotonation of the corresponding acids) in terms of the principle of least nuclear motion, a more drastic reorganization of the structure (i.e. of the atomic positions) being required to go from the carbanion to the acid than is the case for non-delocalized carbanions [24]. Crooks, however, has attributed the slow proton transfer to a delocalized anion such as $[CH_2NO_2]^-$ to the energy required to disrupt the solvation pattern on going from the solvated carbanion to the acid; this effect will be especially marked in the case of $[CH_2NO_2]^-$ since much of negative charge is located on the oxygen atoms, which will be quite strongly hydrogen-bonded to the solvent [24].

However, it is not satisfactory to regard the anions $X{\cdot}C_4H_2S^-$ as having the lone pair of electrons localized at the 2-position. As we have seen, even in the 2-thienyl anion itself, only 25% of the additional negative charge is left at the 2-position according to the calculations, and the same type of calculation shows that 21% is left on the methylene carbon atom in the benzyl anion [25]. In the $5\text{-}O_2N{\cdot}C_4H_2S^-$ anion (with the proton abstracted from the 2-position) only 14% of the negative charge remains at the 2-position **. But the dispersal of the charge in the thienyl anions is not, of course, by a conjugative mechanism, but by inductive and field effects and, more importantly, by polarization of the π-system, and we assume that this involves markedly less disturbance of the skeleton (i.e. changes in bond lengths and angles) than does conjugative delocalization ***. Thus when a proton approaches the 2-position of the 2-thienyl anion, electrons can flow towards that position without any substantial reorganization of the structure, and there is no energy barrier to the protonation.

The explanation offered is based on acceptance of Hine's principle of least nuclear motion. Interpretation in terms of Crook's proposals is less satisfactory, since it should make no difference to the solvation of the partial negative centres whether the charges are dispersed by conjugative or non-conjugative

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* We neglect for present purposes the possibility of some delocalization into the *d*-orbitals of sulphur.

** We suspect that the charge is also extensively dispersed away from the carbanionic centre in anions derived from acids such as disulphones, e.g. $MeCH(SO_2Et)_2$, which are protonated at a very high rate [23,24].

*** Calculations on substituted phenols have recently shown that, in those systems at least, π-charge transfers are energetically more effective than σ-transfers [32].

TABLE 7

APPROXIMATE CALCULATED AND DERIVED pK_a VALUES FOR 2-POSITION OF SUBSTITUTED THIOPHENS

Substituent(s)	Calc. pK_a [a]	Derived pK_a [b]
3-NO_2		15.5
5-NO_2	18	16.5
5-CN		19.5
5-COPh		28.5
4,5-Br_2		22.5
3-Br		26.5
4-Br		29
5-Br		30.5
3-Cl	26	
4-Cl	28	
5-Cl	28	31
5-F	35.5	
None	38.4 [c]	38.4 [c]
5-Me	39	
5-OMe	38	
5-NMe_2	40	

[a] Calculated from ΔE_X values. [b] Derived from log k_s values. [c] Assumed value.

mechanisms. However, the solvation effect may well be of importance in the extreme case of the $[CH_2NO_2]^-$ anion, in which the charge is very largely on the oxygen atoms, and Hine has noted that the principle of least nuclear motion does not satisfactorily account for the very high barrier to protonation of the anions from mono-nitroalkanes and that at least one other factor must operate [23], and this could well be the solvent disruption effect proposed by Crooks [24].

The above observations confirm the value of the cleavages of $RSiMe_3$ species as a source of information about the properties of the carbanionic R^- species.

Acidities of mono-substituted thiophens

Rough pK_a values for the 2-position of X·C_4H_3S compounds can be derived from the calculated deprotonation energies $E_X - E_X^-$ *. The calculated deprotonation energy for cyclopentadiene, which has a pK_a of 15, is −0.7539 a.u. [25]. These data are used along with the pK_a of 38.4 [29] and deprotonation energy of 0.8102 a.u. for thiophen to define an assumed linear relationship between the pK_a's and deprotonation energies, and pK_a's then calculated for the X·C_4H_3S compounds from the $E_X - E_X^-$ data. The values thus obtained are shown in Table 7.

Approximate values for the pK_a's of the X·C_4H_3S compounds can also be derived from the specific rate constants, k_s, for the cleavage of the X·C_4H_2S·$SiMe_3$-2 compounds in MeOH-MeONa by assuming that there is a linear correlation between log k_s and the pK_a. Use of a value of (5 + log k_s) of 4.05 for cleavage of 9-fluorenyltrimethylsilane and a pK_a of 22.7 for fluorene [26] along with a value of (5 + log k_s) of −0.125 for C_4H_3S·$SiMe_3$-2 and a pK_a of

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* Throughout this paper the pK_a values refer to ion-pair acidities in $CsNHC_6H_{11}$-$NH_2C_6H_{11}$ [26,28].

38.4 for thiophen to define the parameters of the relationship, leads to the derived pK_a's listed in Table 7. (No correction was made for the dependence of k_s on NaOMe for the less reactive thienyl compounds, because the effect of this would be insignificant compared with the other uncertainties.) This method cannot be used for the compounds with X = Me, OMe or NMe_2 for reasons which will be clear from the discussion above.

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