Anal. Calcd for $C_9H_{20}OS$: C, 61.33; H, 11.44; S, 18.20; mol wt, 176. Found: C, 61.57; H, 11.60; S, 18.39; mol wt, 176 (mass spectrum, molecular ion).

Reaction of 2,2-Diisopropyl-1,3-oxathiolane with Chlorine. A solution of 17.4 g (0.1 mol) of 2,2-diisopropyl-1,3-oxathiolane in 150 ml of methylene chloride at −70 °C was chlorinated with 7.8 g (0.11 mol) of chlorine according to the procedure previously described. VPC analysis of the solution after the reaction was complete showed the presence of isopropyl ketone and five other products. Quantitative analysis of the product ratio was not possible owing to overlapping of the peaks on the VPC trace. The crude residue was fractionally distilled to give 8.6 g (41%) of major product, bp 85–90 °C (1.0 mm). Repeated distillation of the crude distillate did not remove the impurities. The analytical sample of this product was obtained by column chromatography on 100 g of silica gel using benzene–hexane (3:1) as eluent. The impurities were eluted in the early fractions. The later fractions were combined and concentrated to afford a pure liquid oil identified as α-(2-chloroethylthio)isopropyl isopropyl ketone (**5a**): $n^{25}D$ 1.4821; ν_{max} (neat) 2970, 2940, 2880, 1692, 1468, 1380, 1365, 1035 cm^{-1}; NMR (CCl_4) δ 1.07 (d, J = 7.0 Hz, 6 H), 1.40 (s, 6 H), 2.64 (m, 2 H), 3.42 (m, 2 H); mass spectrum m/e 208 (2.65), 139 (96.25), 137 (66.25), 63 (24.43), 59 (27.08), 43 (100), 41 (92.50), 39 (26.14), 27 (46.78).

Anal. Calcd for $C_9H_{17}OSCl$: C, 51.80; H, 8.21; S, 15.36; mol wt, 208.7. Found: C, 51.78; H, 8.07; S, 16.29; mol wt, 208 (mass spectrum, molecular ion).

Reduction of α-(β-Chloroethylthio)isopropyl Isopropyl Ketone (5a) with Sodium Borohydride. Six grams (28.8 mmol) of **5a** in 50 ml of absolute ethanol was reduced with 2.8 g (73 mmol) of sodium borohydride as previously described. The product, α-ethylthioisopropyl isopropyl alcohol (**6**), after work-up and distillation, was obtained in 77% yield.

Reaction of 1,4-Oxathiaspiro[4.6]undecane with Bromine. A solution of 34.4 g (0.2 mol) of 1,4-oxathiaspiro[4.6]undecane[8] and 33.6 g (0.21 mol) of bromine in 200 ml of carbon tetrachloride was allowed to react as above. After being refluxed for 24 h, the greenish solution was concentrated on the rotary evaporator and the residue was analyzed by VPC which showed mainly cycloheptanone and a small amount of high-boiling material. Distillation of the residue gave 20.7 g (93%) of cycloheptanone, identified by comparisons of the ir spectrum with that of commercial material, and 16.4 g of a gummy residue, apparently a polymeric material.

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Registry No.—1 (R = Ph; X = H), 33735-40-9; 1 (R = *i*-Pr; X = H), 16047-99-7; 1 (R, R = $(CH_2)_6$; X = H), 184-31-6; **2a,** 1002-41-1; **2b,** 1002-40-0; **3,** 119-61-9; **4,** 565-80-0; **5a,** 57738-71-3; **5b,** 57738-72-4; **6,** 57738-73-5; chlorine, 7782-50-5; bromine, 7726-95-6; β-mercaptoethanol, 60-24-2; 1,2,3-oxadithiolane 2-oxide, 57738-74-6; triethylammonium bromide, 636-70-4; cycloheptanone, 502-42-1.

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Kinetics of the Reactions of 2-Bromo-3,5-dinitrothiophene with Meta- and Para-Substituted Anilines in Methanol. The Application of Hammett and Ingold–Yukawa–Tsuno Equations[1a]

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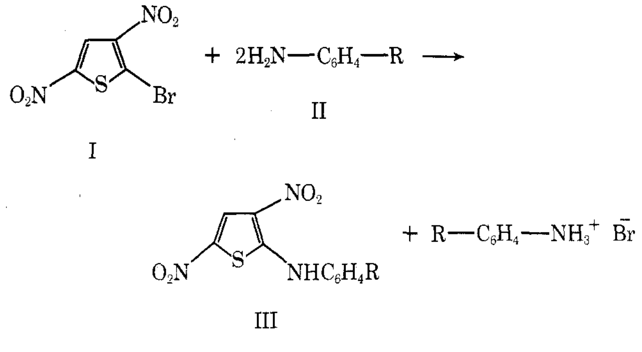
The rate constants of debromination of 2-bromo-3,5-dinitrothiophene by various meta- and para-substituted anilines have been measured in methanol at various temperatures and the Arrhenius parameters determined. The kinetic data have been analyzed, using the Ingold–Yukawa–Tsuno equation. The ρ (−3.00), r^- (0.99), and r^+ (0.38) values obtained are discussed.

The reactions of halogenonitroaromatic and heteroaromatic derivatives with substituted anilines have been studied by many research workers,[2] but no systematic quantitative studies, covering the whole range of substituent effects in the aniline moiety, have so far been carried out.

In the framework of our researches[3] on the applicability of linear free energy relationships to aromatic nucleophilic substitution reactions in the thiophene series, we now report kinetic data of the reaction of 2-bromo-3,5-dinitrothiophene (I) with various meta- and para-substituted anilines (II).

Results

2-Bromo-3,5-dinitrothiophene (I) gave the expected anilino derivatives (III) on treatment with anilines (II) in almost quantitative yields as shown by TLC and uv-visible spectral analysis. The relevant physical and analytical data are shown in Table I.



Rate constants and activation parameters for the anilino debromination reactions of I are shown in Table II. All the reactions were first order both in I and II.[6] An increase of the rate of substitution was observed on introduction of electron-repelling substituents into the nucleophile. On the

Table I. Physical Data for Meta- and Para-Substituted *N*-(3,5-Dinitrothienyl)anilines (III)[a]

Substituent	Registry no.	Color	Crystn solvent	Mp, °C	λ_{max},[b] nm	Log ϵ[b]
p-OCH$_3$[c]	1033-84-7	Orange	Ethanol–dioxane	164[d]	406	4.20
p-CH$_3$[e]	21817-48-1	Orange	Ethanol	146–147	404	4.23
m-CH$_3$[c]	21817-49-2	Red	Ethanol–dioxane	150–151[f]	404	4.24
H[e]	959-38-6	Orange	Ethanol	162–163	402	4.24
p-Cl[c]	19320-18-4	Yellow	Ethanol–dioxane	184–185[g]	396	4.26
p-Br[c]	21817-46-9	Yellow	Ethanol–dioxane	173–174[h]	395	4.24
m-Cl[c]	21817-44-7	Yellow	Methanol–dioxane	193[i]	395	4.25
m-F	57738-59-7	Orange	Ethanol	123–125	396	4.25
m-Br	57738-60-0	Red	Methanol–dioxane	210–211	395	4.24
p-CO$_2$CH$_3$	57738-61-1	Yellow	Ethanol–dioxane	189–190	390	4.32
m-NO$_2$	57738-62-2	Red	Ethanol–dioxane	202	386	4.26
p-COCH$_3$	57738-63-3	Yellow	Ethanol–dioxane	196–197	394	4.35
p-CN	57738-64-4	Orange	Ethanol–dioxane	219–220	388	4.38
p-NO$_2$[e]	30514-82-0	Red	Ethanol–dioxane	210	396	4.45

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for all new compounds listed in the table. [b] In methanol. [c] See ref 4. [d] Lit. mp 158 °C. [e] See ref 5. [f] Lit. mp 148 °C. [g] Lit. mp 180 °C. [h] Lit. mp 172.5–173 °C. [i] Lit. mp 185–186 °C.

Table II. Rate Constants and Activation Parameters for the Reactions of 2-Bromo-3,5-dinitrothiophene (I) with Substituted Anilines (II) in Methanol

No.	Substituent	Registry no.	$10^3 k$, l. mol^{-1} s^{-1} (at various temperatures)[a]			$\Delta H^‡$,[b] kcal mol^{-1}	$-\Delta S^‡$,[c] cal mol^{-1} K^{-1}
1	p-OCH$_3$	104-94-9	304 (9.99)	521 (20.10)	796 (29.97)	7.6	33.7
2	p-CH$_3$	106-49-0	44.0 (0.05)	83.1 (10.08)	141 (20.05)	8.7	32.7
3	m-CH$_3$	108-44-1	64.6 (20.04)	107 (29.95)	178 (39.95)	8.7	34.3
4	H	62-53-3	12.2 (0.02)	23.0 (10.02)	41.9 (20.05)	9.2	33.4
5	p-Cl	106-47-8	9.40 (20.10)	16.5 (29.96)	27.3 (39.95)	9.2	36.3
6	p-Br	106-40-1	7.75 (19.76)	13.9 (30.02)	23.6 (40.05)	9.4	36.0
7	m-Cl	108-42-9	3.23 (19.95)	5.89 (30.00)	10.3 (40.02)	9.9	36.0
8	m-F	372-19-0	3.15 (20.10)	5.64 (29.98)	9.96 (40.01)	9.9	36.0
9	m-Br	591-19-5	3.08 (20.02)	5.72 (30.01)	10.1 (40.20)	10.1	35.4
10	p-CO$_2$CH$_3$	150-13-0	0.361 (20.03)	0.717 (30.00)	1.37 (40.08)	11.6	34.7
11	m-NO$_2$	99-09-2	0.278 (19.92)	0.524 (30.00)	0.951 (40.02)	10.6	38.7
12	p-COCH$_3$	98-86-2	0.215 (19.94)	0.429 (30.00)	0.88 (40.20)	12.1	33.9
13	p-CN	873-74-5	0.0627 (24.91)	0.126 (34.92)	0.254 (45.08)	13.1	35.9
14	p-NO$_2$	100-01-6	0.0114 (25.03)	0.0285 (34.93)	0.0716 (45.00)	17.3	25.0

[a] The rate constants are accurate to within ±3%. [b] At 20 °C, the maximum error is 0.5 kcal mol^{-1}. [c] At 20 °C.

other hand, the electron-attracting substituents markedly reduced the reaction rate with respect to hydrogen. The reactions studied were controlled by the enthalpy, and the nearly constant values of their activation entropy agree with the accepted mechanism[2b,7] (bimolecular, with large solvent participation in the transition state, and probable hydrogen bond formation).

Discussion

Hammett Relationship. The correlation of the reactivity data with Hammett substituent constants,[8] although giving, as expected, a negative ρ value, was not satisfactory (Table III). An examination of the Hammett plot (Figure 1) indicates that the para substituents notably deviate from the straight line for meta-substituted anilines ($\rho_{meta} = -3.03$).

Ingold–Yukawa–Tsuno (IYT) Relationship. It is generally recognized[9] that the Hammett relationship fails when a ±M substituent can interact with a reaction center ∓M in para position. In order to cover the deviations from the Hammett relationship observed for the para substituents, we have made use of the Ingold–Yukawa–Tsuno equation[10,9d]

$$\log k/k_H = \rho(\sigma^n + r^-\Delta\sigma_R^- + r^+\Delta\sigma_R^+)$$

Such a multiparameter treatment requires (a) a sufficient number (at least four) of *good* meta substituents and hydrogen, (b) a suitable number (at least four) of electron-withdrawing and/or -attracting substituents, and (c) a suitable number (at least four) of electron-donating and/or -repelling substituents.

The kinetic data at 20 °C related to meta-substituted anilines gives a good correlation (Table III) with σ^n values and the ρ value obtained can be utilized to calculate r^- and r^+ coefficients by means of the equations

$$\sigma - \sigma^n = r^\pm\Delta\sigma_R^\pm$$

where σ is the observed substituent parameter. The correlation of $\sigma - \sigma^n$ versus $\Delta\sigma_R^\pm$ gives, respectively, $r^- = 0.99 \pm 0.14$ ($R = 0.972$; $n = 5$) and $r^+ = 0.38 \pm 0.01$ ($R = 0.999$; $n = 5$). The least-squares line pertaining to the "*overall*" IYT equation ($\rho = -3.00$) is shown in Figure 2 and the relevant statistical data are reported in Table III.

The reasons of the deviations from a simple Hammett relationship for the anilines with electron-attracting para substituents and the consequent necessity of using an additive term, i.e., $r^-\Delta\sigma_R^-$, are evident on account of the definition of σ^- values by the anilinium cations dissociation reaction.[9d] Moreover, the necessity for using the term $r^+\Delta\sigma_R^+$ to cover the deviations due to the electron-repelling para substituents arises from the polarization of these substituents operated by the "ammonium" nitrogen in the rate-determining transition state.

Figures 1 and 2 show the considerable improvement in the linearity of the plot of log k against substituent parameter when the appropriate σ^+ and σ^- contributions are included. The value of the coefficient r^- points out that in the transition state the formation of the bond between

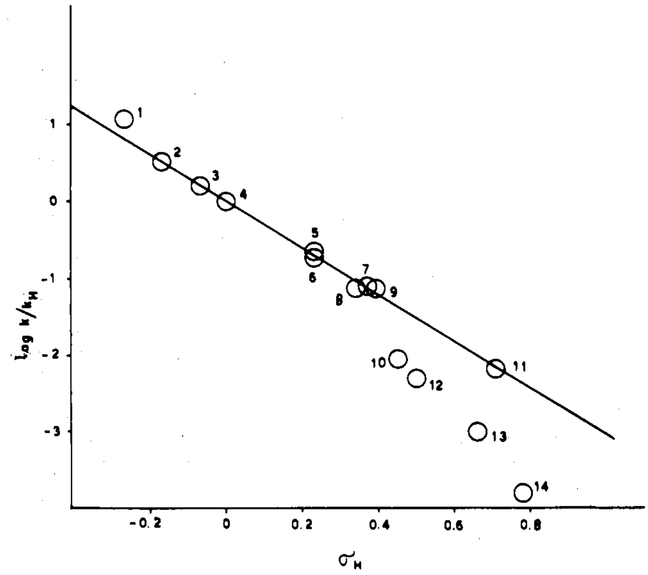


Figure 1. Hammett plot for anilino debromination reactions; the straight line refers to meta-substituted anilines ($\rho_{meta} = -3.03$).

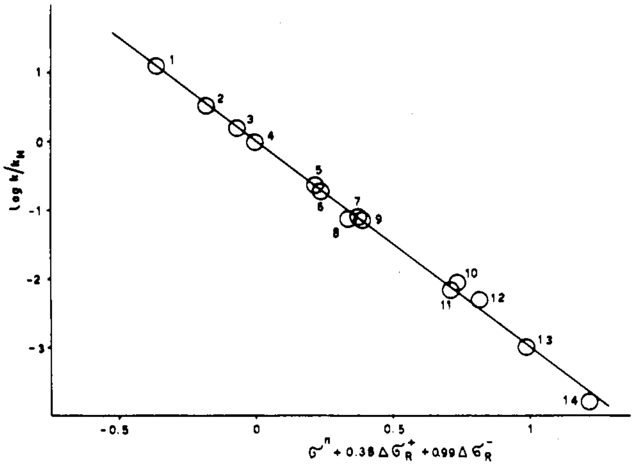


Figure 2. Least-squares line pertaining to the "overall" IYT equation ($\rho = -3.00$).

amino nitrogen and nuclear carbon of 2-bromo-3,5-dinitrothiophene has proceeded to a marked extent, i.e., the proclivity of the lone pair electrons on nitrogen to interact with the electron-attracting para substituents is significantly reduced in the transition state compared with that in the reactants.[14]

The observed necessity of using both r^+ and r^- contributions in the anilino debromination reaction induced us to apply the same treatment of data to the acid–base equilibrium of $ArNH_3^+$ in water, at 25 °C. The IYT analysis including only the substituents studied by us gives the values $\rho = -2.93 \pm 0.04$ ($R = 0.9991$; $n = 14$), $r^- = 1.00 \pm 0.04$ ($R = 0.9978$; $n = 5$; $i = 0.00 \pm 0.01$), and $r^+ = 0.23 \pm 0.04$ ($R = 0.9643$; $n = 5$; $i = -0.02 \pm 0.01$), closely resembling those observed by us for the anilino debromination reaction (see Table III). According to our interpretation of the ρ values,[3b] this means that the substituents present in aniline cause a similar variation of the position of the transition state in the reaction coordinates, with respect to X = H, for the reactions considered (see also below). On the other hand, the similar r^+ and r^- values obtained indicate a simi-

Table III. Linear Free Energy Relationships[a] for the Reaction of 2-Bromo-3,5-dinitrothiophene (I) with Meta- and Para-Substituted Anilines in Methanol at 20 °C and for the Dissociation of Anilinium Ions in Water at 25 °C

Relationships	$\rho \pm s_\rho$	s	R	i	Substituents
$\log k/k_H = \rho\sigma_H$	−4.10 ± 0.32	0.37	0.9660	0.06	1–14
$\log k/k_H = \rho\sigma^n$	−3.03 ± 0.09	0.06	0.9981	−0.01	3, 4, 7, 8, 9, 11
$\log k/k_H = \rho\,(\sigma^n + 0.38\Delta\sigma_R^+ + 0.99\Delta\sigma_R^-)$	−3.00 ± 0.05	0.08	0.9983	0.00	1–14
$\Delta pK_a = \rho\sigma^n$	−2.89 ± 0.10	0.06	0.9975	−0.02	3, 4, 7, 8, 9, 11
$\Delta pK_a = \rho(\sigma^n + 0.23\Delta\sigma_R^+ + 1.00\Delta\sigma_R^-)$	−2.93 ± 0.04	0.06	0.9991	0.02	1–14
	$\beta \pm s_\beta$				
$\log k/k_H = \beta\Delta pK_a$	1.05 ± 0.03	0.05	0.9986	0.01	3, 4, 7, 8, 9, 11
$\log k/k_H = \beta\Delta pK_a$	1.05 ± 0.02	0.11	0.9968	0.06	1–14

[a] ρ, reaction constant; β, Bronsted constant; s_ρ, standard deviation of ρ; s_β, standard deviation of β; s, standard error of estimate; R, correlation coefficient; i, intercept of the regression line with the ordinate [σ (or ΔpK_a) = 0]; substituents, actual substituents involved in the calculation of ρ and β, identified according to their number mentioned in Table II. The values of σ_H, σ^n, $\Delta\sigma_R^+$, $\Delta\sigma_R^-$, $\log k/k_H$, and pK_a used in correlations are shown in Table IV.

Table IV. Parameters Involved in the Calculation of ρ and β Values

Substituent	σ_H[a]	σ^n [b]	$\Delta\sigma_R^+(\Delta\sigma_R^-)$[b]	Log k/k_H[c]	σ[d]	pK_a[e]	σ[f]
1	−0.268	−0.09	−0.71	1.086	−0.36	5.36	−0.27
2	−0.170	−0.10	−0.22	0.534	−0.18	5.08	−0.18
3	−0.069	−0.069		0.188		4.71	
4	0.000	0.000		0.000		4.59	
5	0.227	0.29	−0.19	−0.647	0.21	3.98	0.20
6	0.232	0.30	−0.16	−0.724	0.23_5	3.89	0.23_5
7	0.373	0.373		−1.109		3.52	
8	0.337	0.337		−1.125		3.57	
9	0.391	0.391		−1.130		3.53	
10	0.45[g]	0.46	0.28	−2.063	0.68	2.38	0.76
11	0.710	0.710		−2.174		2.46	
12	0.502	0.502	0.32	−2.290	0.75	2.19	0.82
13	0.660	0.70	0.29	−2.986	0.98	1.74	0.98
14	0.778	0.778	0.45	−3.785	1.25	1.02	1.23

[a] σ values defined by L. P. Hammett,[8a] from ref 8b. [b] Values from ref 9d. [c] From k's calculated at 20 °C by the activation parameters. [d] Calculated for the anilino debromination reaction as in ref 9c. [e] Values from ref 11–13. [f] Calculated for the anilinium ions dissociation as in ref 9c. [g] Value for p-$CO_2C_2H_5$.

lar sensitivity of the two reactions to the changes in the nucleophilicity (polarizability) of the nitrogen atom as a function of the substituent present in the aniline moiety.

The log (k/k_H) for the anilino debromination reaction gives, for these reasons, a good correlation with ΔpK_a of $ArNH_3^+$ in water (see Tables III and IV). Even if the comparison between the two reactions is not completely homogeneous because of the difference in the solvent, the β value, near to unity, expresses the above-mentioned similarity of the two reactions; in consideration of other recent observations,[16] we do not think that it has any other physical meaning.

Experimental Section

Materials. 2-Bromo-3,5-dinitrothiophene was prepared and purified as previously reported.[17] Commercial samples of anilines were purified by crystallization or distillation under reduced pressure. The anilino derivatives were prepared and purified according to the general method reported in ref 5. The melting points, the crystallization solvents, and the analytical data are shown in Table I.

Kinetic Procedure. The kinetics were followed spectrophotometrically as previously described.[7b] The concentrations employed were 10^{-4}–10^{-3} M for 2-bromo-3,5-dinitrothiophene and 6×10^{-4} to 4×10^{-2} M for anilines as a function of their nucleophilicity. The rate constants for the *p*-nitroanilino debromination were determined by titration of the acid produced with 10^{-2} N sodium hydroxide, using a PHM 63 digital pH meter, *p*-nitroaniline at the wavelength of the maximum absorption of *p*-nitroanilino derivative having a high extinction coefficient.

The reaction of I with *p*-carbomethoxyaniline has been chosen to compare both kinetic procedures: the kinetic constants obtained by both methods are in excellent agreement.

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Registry No.—I, 2160-38-5.

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(14) It seems likely that the degree of bond formation, as measured by r^-, is a function of the reactivity of the aromatic substrate. In fact the r^- value (0.68) for the reaction of picryl chloride with substituted anilines in 75% ethanol at 30 °C[2b] is lower than for the less reactive 2-bromo-3,5-dinitrothiophene. Taking into account that both reaction series are isoentropic and display much the same value of $\Delta S^\ddagger$, the trend of r^- values is in line with predictions from the Hammond postulate.[15]

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