Degradation in Aqueous Solution of *O*-Aryl *N*-Arylthioncarbamates to Aryloxide Ions and Isothiocyanates. A Study of Leffler's Assumption [1a]

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Rate constants for the title reaction have been measured in both forward and reverse directions leading to rates and equilibrium constants for all the steps in equation (i). The effects of varying the structures of Ar

$$\mathrm{Ar{-}O{-}CS{-}NHAr'} \rightleftharpoons \mathrm{Ar{-}O{-}C\bar{S}N{-}Ar'} \rightleftharpoons \mathrm{Ar{-}O^-} + \mathrm{Ar'NCS} \qquad \text{(i)}$$

and Ar' on the equilibrium and rate constants were measured; identical Leffler–Grunwald indices ($\alpha = \beta_F/\beta_{EQ} = \mathrm{d}\log k/\mathrm{d}\log K$) for the addition step are observed for variation in Ar and Ar' although individual β values are markedly different. Identical α parameters arising from different substituent interaction pathways to a single bond are required if the reaction conforms to the Leffler assumption; on this basis the α parameter is considered a good measure of transition-state structure relative to reactant- and product-states for the addition reaction. 'Effective charges' on the phenolic oxygen in the thioncarbamate and its conjugate base indicate considerable $C^+{-}S^-$ character in the formal thioncarbamoyl bond.

Leffler [1,2] assumed that changes in the free energy of a transition state can be represented as a linear combination of corresponding changes in reactant- and product-states in a single step reaction. If this assumption is correct for a particular reaction the structure of the transition state may be measured [1] by the parameter α [equation (1)] where β_F and β_{EQ} are Brønsted sensitivities for the forward rate constant and the overall equilibrium constant. The value of α may be estimated easily for proton transfer reactions but these are often associated with 'heavy' atom reorganisations and the Leffler assumption will not then necessarily be valid.[3a] For reactions

$$\alpha = \beta_F/\beta_{EQ} = \mathrm{d}\log k/\mathrm{d}\log K \qquad (1)$$

where only bonds to heavy atoms are involved the difficulty of measuring accurate equilibrium constants and the variation of these with substituents has hampered research into the significance of the α parameter; it has moreover encouraged the use of simple β_N or β_L values as indices of transition-state structure. The calibrating equilibrium for the latter, namely the ionisation of an acid, usually has no similarity to the reaction in hand making a β value a highly suspect index of transition-state structures if used alone.

If the Leffler assumption is valid the α parameters obtained through variation of substituents through *two* interacting paths to the *same* reacting bond are required to be identical. That is, the electronic change in a bond 'seen' through substituent effects from any direction should be the same. Clearly it is very hard to find a system to demonstrate such an equality because of difficulties in measuring equilibrium constants. We are fortunate in that the rate and equilibrium constants for addition of aryloxide ions to aryl isothiocyanates [equation (2)] may be easily measured. The addition step has very little

$$\mathrm{Ar{-}O^-} + \mathrm{Ar'NCS} \rightleftharpoons \mathrm{Ar{-}O{-}C\bar{S}N{-}Ar'} \rightleftharpoons \mathrm{Ar{-}O{-}CS{-}NH{-}Ar'} \qquad (2)$$

atomic reorganisation above that of the bond forming between oxygen and carbon. Variation of substituents in the *N*- and *O*-aryl groups monitor the electronic changes in the carbon–oxygen bond and two α parameters may be derived.

Experimental

Materials.—*O*-4-Methoxyphenyl chlorothioformate was prepared by adding a solution of 4-methoxyphenol (8.3 g, 67 mmol) in 5% NaOH (60 ml) dropwise to a well stirred, cooled solution of thiophosgene (7.7 g, 67 mmol) in chloroform (40 ml). The reaction was stirred for 1 h at 0—5° and the chloroform layer washed with dilute HCl and water. The chloroform solution was dried with sodium sulphate, evaporated, and the residue distilled to yield a liquid, b.p. 92° at 0.5 Torr (lit.,[3b] 141—143° at 13 Torr), which solidified on cooling.

O-4-Methoxyphenyl *N*-arylthioncarbamates were prepared by adding the aniline (32 mmol) dissolved in carbon tetrachloride (5 ml) to a stirred, cooled solution of *O*-(4-methoxyphenyl) chlorothioformate (3.3 g, 10 mmol) in carbon tetrachloride (50 ml). The mixture was stirred at room temperature for 24 h, filtered, and the filtrate evaporated to dryness. The thioncarbamate was recrystallised from a suitable solvent (see Table 1).

Aryl isothiocyanates were prepared by adding a slight excess of thiophosgene to a mechanically stirred mixture of the appropriate aniline and water. Reaction was almost instantaneous and the isothiocyanate separated as an oil and was extracted with ether. The ether was dried (Na_2SO_4), evaporated, and the residual oil distilled under high vacuum.

The materials prepared above had satisfactory analyses (Table 1) and their structures were confirmed by i.r. (Perkin-Elmer 297 instrument) and 100 MHz ^{1}H n.m.r. spectra. The latter spectra were recorded by Dr. D. O. Smith using a JEOL instrument. Buffers and reagents used in the kinetics were of analytical quality or were recrystallised or redistilled from bench grade materials. Water used throughout the investigation was distilled twice from glass.

Methods.—Kinetics were followed spectrophotometrically at an appropriate wavelength determined using a repetitive wavelength scanning spectrophotometer (Unicam SP 800). Constant wavelength studies were carried out using a Unicam SP 800 machine or a Beckman D.B. instrument fitted with Servoscribe potentiometric recorders. The stock solution of substrate (thioncarbamate or isothiocyanate) in ethanol or

Table 1. Analytical and physical properties of substrates

		Analysis [a]						
		Found (%)				Requires (%)		
Aryl substituent	M.p. (°C) [c]	C	H	N	Formula	C	H	N
O-(4-methoxyphenyl) *N*-arylthioncarbamates [b]								
4-Methyl	114—115	66.0	5.6	5.2	$C_{15}H_{15}NO_2S$	65.9	5.5	5.1
4-Chloro	161—162	57.5	4.1	4.9	$C_{14}H_{12}ClNO_2S$	57.2	4.1	4.8
3-Chloro	122—123	57.4	4.0	4.8	$C_{14}H_{12}ClNO_2S$	57.2	4.1	4.8
2-Chloro	124—125	57.1	4.2	4.8	$C_{14}H_{12}ClNO_2S$	57.2	4.1	4.8
2,5-Dichloro	131—132	51.3	3.1	4.3	$C_{14}H_{11}Cl_2NO_2S$	51.2	3.4	4.3
3-Nitro	139—141	55.4	3.6	9.1	$C_{14}H_{12}N_2O_4S$	55.3	4.0	9.2
O-aryl *N*-phenylthioncarbamates								
3-Chloro	124—125	59.4	3.8	5.3	$C_{13}H_{10}ClNOS$	59.2	3.8	5.3
4-Methyl	155—156	69.4	5.5	5.7	$C_{14}H_{13}NOS$	69.1	5.4	5.8
2,4-Dimethyl	159—162	70.3	6.0	5.5	$C_{15}H_{15}NOS$	70.0	5.9	5.4

[a] Analyses by Mr. A. Fassam using a Carlo Erba CHN analyser. [b] Recrystallised from benzene. [c] M.p.s determined with a Kofler Thermospan instrument.

acetonitrile (50 µl) was placed on the flattened tip of a glass rod and introduced into the buffer (2.5 ml) in a silica cell in the thermostatted cell compartment of the spectrophotometer. Two or three rapid vertical ' pumping ' motions ensured rapid and complete mixing and the trace on the recorder was activated at the instant the glass rod entered the solution. The pH was measured before and after the reaction using a Radiometer pH-meter PHM 26 calibrated with E.I.L. buffers to ±0.01 units. Traces of absorbance were analysed by plotting $A_t - A_\infty$ *versus* time on two cycle semi-logarithmic graph paper. Reactions obeying first-order rate laws gave linear plots; where the absorbance trace gave evidence of an intermediate the decay rate constant (λ_2) was sufficiently different from that for formation (λ_1) to enable separate measurement.

The measurement of fast reactions was carried out using rapid mixing apparatus similar to that devised by Perlmutter-Hayman and Wolff.[4] The apparatus comprised a Unicam SP 500 monochromator, a Hamilton springloaded syringe (CR 700-200 with microswitch) which squirted a portion (*ca.* 100—200 µl) of stock solution to the centre of a cylindrical silica cell, a photomultiplier (RCA IP28) with a Farnell Instruments (EI) stabilised high voltage power supply, and a recording oscilloscope (Telequipment DM 64). A Polaroid CR9 Land oscilloscope camera was used to record selected traces.

The springloaded syringe was fitted with a 19 HL gauge needle possessing a rounded tip and rested in a screw sleeve in a thermostatically controlled brass block. A 3.0 ml capacity silica cuvette of 22 mm diameter and 10 mm path length (Hellma Ltd.) fitted within the block which was screwed to the face of the SP 500 to accept the monochromatic light beam. The photomultiplier was housed in a brass block which fits to the side of the cell block away from the monochromator to accept the transmitted signal. Access to the cell block was facilitated by the provision of a hinge to enable the photomultiplier to swing back from the cell housing. The syringe rested in the block so that the needle was centrally located while the light beam passed off-centre. The height of the needle orifice in the cell was critical and was adjusted by the screw sleeve till the mixing was judged to be most rapid from trial experiments. The output of the photomultiplier was recorded directly on the storage oscilloscope and the trace was triggered by a voltage supplied from the syringe trigger microswitch. Optimum mixing conditions were found to be when the orifice of the needle rested approximately 3—4 mm from the bottom of the cuvette which was filled almost to its neck and when 100—200 µl stock solution were added. The aqueous buffer was degassed before use with an Edwards high vacuum pump.

The oscilloscope was calibrated by injecting a decay voltage from an RC circuit which possessed an accurately scaled resistor. Photographs of the traces were made with the camera and the time constant for these traces obtained for the expanded image of the negatives (a regular photographic enlarger was used to display the negatives onto graph paper). The time constants were plotted *versus* the scale setting on the resistor to give a calibration curve. To measure the time constant for a reaction the stored trace on the oscilloscope was transferred to a plastic sheet using a narrow marker pen; the original trace was erased and the decay voltage from the RC circuit was displayed. The resistance was adjusted till the injected trace coincided with that from the recorded reaction (appropriate vertical and horizontal adjustments are also necessary). The reading of the resistance scale coupled with the calibration curve gives the pseudo-first-order rate constant for the reaction[5] with an error well within the 5% normally accepted by us as reasonable.

Results

Hydrolysis of Thioncarbamates in Buffers.—The degradation of aryl thioncarbamates in aqueous buffers liberates the isothiocyanate and phenol.[6] At high pH the isothiocyanate decomposes and at a suitable wavelength the intermediate can be observed to form and decay as illustrated for *O*-4-methylphenyl *N*-phenylthioncarbamate (Figure 1). The rate constant for decay (λ_2) of the intermediate from the *O*-4-methoxyphenyl *N*-3-chlorophenylthioncarbamate at pH 11.77 (2.98×10^{-3} s^{-1}) agrees well with that for decay of the synthetic isothiocyanate (2.95×10^{-3} s^{-1}). The formation rate constant (λ_1) was always sufficiently large in the pH region of interest compared with λ_2 that special computational methods were not needed in its evaluation. Since the amount of phenol liberated in the formation of isothiocyanate is never large, the reverse reaction can be neglected (except where phenol is added) and λ_1 is therefore equal to k_1' and λ_2 to k_2 in equation (3). The reactivity data are in good agreement with those of Sartore *et al.* on thioncarbamate degradation.[6]

Table 2. Data for the alkaline degradation of *O*-4-methoxyphenyl *N*-arylthioncarbamates [a]

Substituent	N [c]	pK^{NH}	λ_k/nm	$10^{-2}\,k_1/s^{-1}$	pH [d]	k_{OH}/l mol^{-1} s^{-1} (ArNCS) [k]
4-Methyl [f]	10	9.40	283	5.1	9—11.5	
Unsubstituted	14	9.25	290	6.0	7—11.5	0.13 [b] (6)
4-Chloro	9	8.75	283	2.6	8.5—11.5	0.42
3-Chloro	9	8.52	243	2.2	7.5—10.5	0.36 [b] (5)
2-Chloro	22	7.95	287	1.2	7.5—9	0.71
2,5-Dichloro	6	7.2	280	0.61	7.5—10.1	1.2
3-Nitro	13	7.9	280	1.1	7.2—8.8	1.5
4-Nitro [e]			358			1.9 [b]

[a] 25°, ionic strength kept at 0.1M with KCl. [b] Data from synthetic ArNCS; figures in parentheses are numbers of points. [c] Number of data points. [d] Range of pH studied. [e] The *N*-4-nitrophenylthioncarbamate was not studied. [f] At pH 8.9, 25°, and ionic strength 0.1M the pseudo-first-order rate constants for isothiocyanate formation are: 0.012, 0.0124, 0.0120, and 0.0126 s^{-1} at respectively 0.04, 0.06, 0.08, and 0.1M-trishydroxymethylaminomethane buffer. [k] These results obey the Brønsted type law $\log k_{OH} = -0.3\, pK^{ArNH_3} + 0.65$.

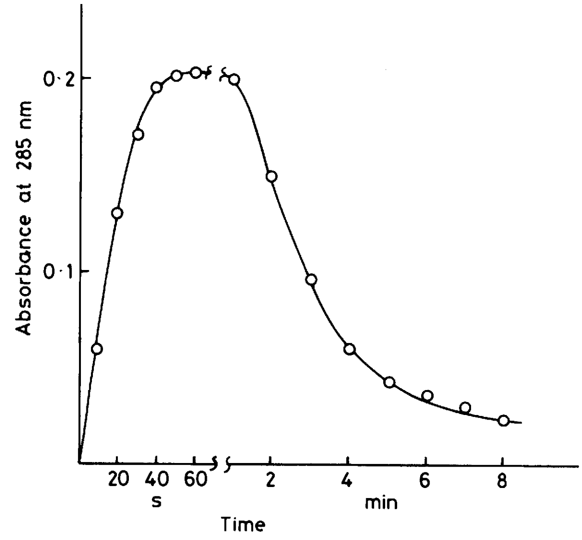


Figure 1. Decomposition of *O*-4-methoxyphenyl *N*-phenylthioncarbamate in 0.1M-KOH at 25 °C and ionic strength made up to 0.1M with KCl. The line is theoretical from rate parameters given in Table 2

$$\text{Ester} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{ArO}^- + \text{Ar'NCS} \xrightarrow{k_2} \text{products} \qquad (3)$$

The formation (λ_1) and decay (λ_2) reactions follows good pseudo-first-order kinetics and are not buffer catalysed in the range of pH investigated as expected from the results in ref. 6. The formation rate constant (λ_1) follows a sigmoidal pH-dependence [equation (4); see for example Figure 2]. The ionisation constant (K_a) was not measured directly for the

$$k_1' = k_1/(1 + a_H/K_a) \qquad (4)$$

thioncarbamates owing to the very rapid hydrolysis but the values obtained kinetically (Table 2) are close to those measured by Calmon [6] and Vecera.[7]

The degradation of isothiocyanates in buffers follows good first-order kinetics with rate constants proportional to the hydroxide ion concentration; the derived second-order rate constants (Table 2) agree with those of previous work [8-11] and fit a Brønsted equation given in Table 2. Most of the rate constants are from isothiocyanates generated *in situ* from the thioncarbamate.

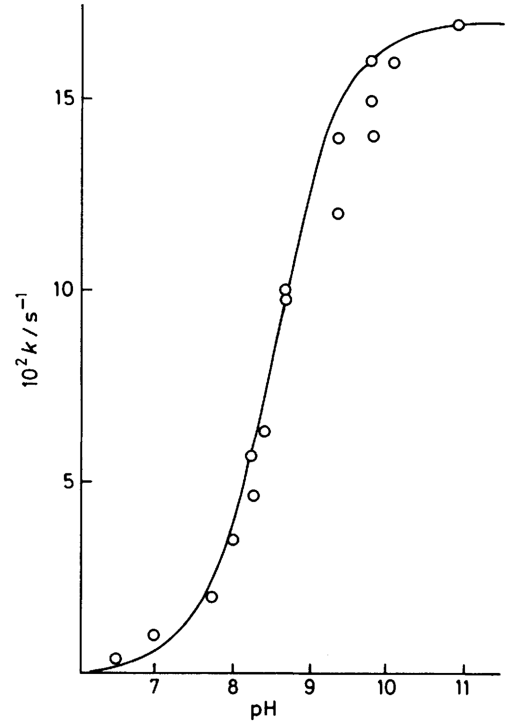


Figure 2. Dependence on pH of the formation of the intermediate ($k = \lambda_1$) from *O*-4-chlorophenyl *N*-phenylthioncarbamate measured at 25° and ionic strength made up to 0.1M with KCl. The line is theoretical from parameters given in Table 4

Degradation of Isothiocyanates in Phenolate Buffers.—Isothiocyanates undergo an initial rapid degradation (λ_3) in phenolate buffer followed by a slower degradation (λ_4) essentially the hydrolysis reaction. Pseudo-first-order rate constants for the initial reaction are linearly dependent on the phenolate ion concentration. A typical example is shown in Figure 3 for 4-nitrophenyl isothiocyanate in phenol buffers. The background hydrolysis of the isothiocyanate (catalysed by hydroxide ion) is negligible compared with the observed rate constants and we propose that the approach to equilibrium with thioncarbamate ester is being measured [equation (5)] in the initial step. The theoretical rate law for approach to equilibrium is thus the sum of forward and reverse rate constants [equation (6)]. We can test conformity with this equation easily because we can obtain k_1 from separate studies of the decomposition of independently synthesised thion-

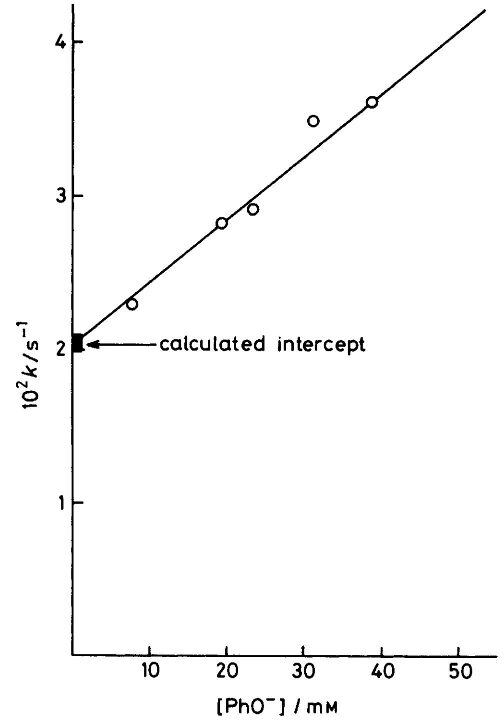


Figure 3. The decomposition of 4-nitrophenyl isothiocyanate in 0.05M-borate buffer at pH 9.86 containing phenol at FB 0.45 ($k = \lambda_3$). Reaction followed at 358 nm, 25°, and 0.1M ionic strength. The rate constant calculated from hydrolysis of the isothiocyanate is 1.6×10^{-3} s^{-1} and that calculated for the decomposition of *O*-phenyl *N*-4-nitrophenylthioncarbamate (data in Table 3) at pH 9.86 is 2.1×10^{-2} s^{-1} (shown as a filled square)

$$\text{Ar'NCS} + \text{ArO}^- \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \text{Ar'N}\bar{\text{C}}\text{SOAr} \qquad (5)$$

carbamate. In the case of the *O*-phenyl *N*-4-nitrophenylthioncarbamate the calculated intercept (k_1) coincides nicely with the observed (see Figure 3) and we therefore feel justified

$$\lambda_3 = k_{-1}[\text{ArO}^-] + k_1 \qquad (6)$$

in using this approach to measure the synthetic rate constant (k_{-1}) from the slope of the plot of λ_3 *versus* [PhO$^-$]. We should add that the observed changes in rate constant are significant over such small changes in phenolate ion concentration and that we are working at pH values well above the pK^{NH} values of the thioncarbamates in question. The strong absorbance of the phenols is accentuated by the necessity to have them present at relatively high concentration and we are therefore restricted to studies on isothiocyanates which have absorbance changes well towards the visible end of the u.v.

We are able to make a further independent check by observing the decay of 4-nitrophenyl isothiocyanate in phenolate buffers where comparison of the decreased rate constants with those predicted from the equilibrium constants for thioncarbamate formation calculated from the ratio of the rate constants shows relatively good agreement (Figure 4). These experiments were carried out at pH 11.48 because at the lower pH the decomposition of phenol interfered over the long time period needed to observe isothiocyanate decay. A further independent check of the method involved observing the rate constant for degradation of *O*-phenyl *N*-4-nitrophenylthioncarbamate in phenolate buffers; here the rate constant for the slower change (λ_4) gave an excellent fit to the decay of 4-nitrophenyl isothiocyanate in the same phenolate concentration at the same pH (see Figure 4).

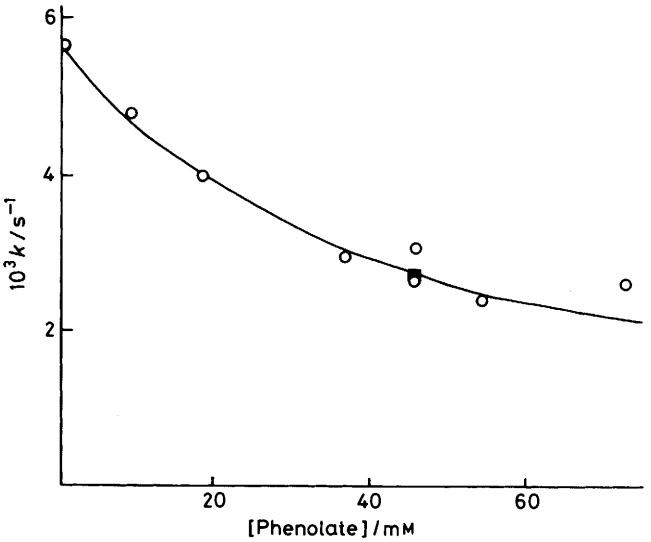


Figure 4. The decomposition of 4-nitrophenyl isothiocyanate ($k = \lambda_4$, open circles) at pH 11.48 in phosphate buffer (0.01M) containing phenol. Reaction followed at 358 nm, 25°, and 0.1M ionic strength. The line is theoretical calculated for the fraction of substrate present as the isothiocyanate using the equilibrium constant determined kinetically (see Results section). The decomposition of the thioncarbamate (λ_4) is shown by the filled square

Table 3. Reaction of phenolate anion with substituted nitrophenyl isothiocyanates [a]

Substituent	N [c]	k_{-1}/ l mol^{-1} s^{-1}	$10^2 k_1$/ s^{-1}	pH [d]
2-Nitro	6	1.2	1.4	10.01
3-Nitro	4	0.24	2.4	10.01
4-Nitro	5	0.48	1.9 [b]	9.86
2-Methyl-5-nitro	4	0.26	1.2	10.30

[a] 25°, ionic strength maintained at 0.1M with KCl, with borate buffer 0.05M. [b] The value of k_1 derived from direct hydrolysis of the thioncarbamate (pH 6.5—10.7 in nine points) is 2.1×10^{-2} s^{-1}; the pK^{NH} from the hydrolysis experiments is 7.50. [c] Number of data points. [d] pH of reaction.

A final check on the kinetic method for determining the equilibrium constant involves a knowledge of the extinction coefficients of 4-nitrophenyl isothiocyanate, phenol, and *O*-phenyl *N*-4-nitrophenylthiocarbamate at pH 11.48, 25°, and 0.1M ionic strength. These were measured at 358 nm extrapolating to zero time to allow for hydrolysis; phenol has negligible absorption and the molar extinction coefficients for isothiocyanate and thioncarbamate are, respectively, 4 680 and 8 300. An experiment was carried out where 4-nitrophenyl isothiocyanate was added to phosphate buffer (0.01M) containing phenolate ion at pH 11.48. The characteristic 'biphasic' reaction occurred and the logarithmic plot for λ_4 was extrapolated to zero time to give the absorbance due to the 'equilibrium' composition. The absorbance at 358 nm may be estimated to be 0.62 from the concentrations of isothiocyanate and thioncarbamate calculated from the equilibrium constant from the kinetic studies ([4-MNO$_2$C$_6$H$_4$NCSO-

Table 4. Degradation of *O*-aryl *N*-phenylthioncarbamates in alkali [a]

Substituent	N [b]	pK^{NH}	pH [c]	$10\ k_1$/ s^{-1}	10^{-3} k^{OH} [f]
Unsubstituted [e]		9.04		1.04	9.4
4-Methoxy [d]		9.25		0.40	2.2
4-Methyl	6	9.28	8.3—11.1	0.47	2.4
4-Chloro	17	8.5	6.5—10.9	1.8	56
3 Chloro	16	8.32	6.0—11.1	4.5	220
4-Acetyl [e]					410
3-Acetyl [e]					160

[a] 25°, ionic strength maintained at 0.1M with KCl. [b] Number of points. [c] pH range. [d] Data (from Table 2) agrees closely with data from ref. 6. [e] From ref. 6 (at 0.1M ionic strength). [f] $k_{OH} = k_1K^{NH}/K_w$.

Table 5. Reaction of aryloxide ions with 3-nitrophenyl isothiocyanate [a,b]

Phenol substituent	N [c]	10^2 k_{-1}/ $l\ mol^{-1}$ s^{-1}	$10^2\ k_1$/ s^{-1}	pH [d]
Unsubstituted	4,3,4	23	2.3	10.01 10.43, 10.82
2,4-Dimethyl	5,5	88	0.24	10.57, 10.94
2,6-Dimethyl	4,3	31	0.18	10.55, 10.76
2,4,6-Trimethyl	5	100	0.2	11.18
4-Methyl	5,4	33	1.1	10.78, 10.08
2,5-Dimethyl	5	66	0.32	10.76
2,3-Dimethyl	5	71	0.32	10.75
2-Methyl	6	53	0.55	10.78
3-Methyl	5	26	1.8	10.95

[a] 25°, ionic strength maintained at 0.1M with KCl. [b] Reactions carried out at pH values above the pK of the NH group of the product thioncarbamate and we thus do not have pK^{NH} data. [c] Number of points. [d] pH of the experiments.

Table 6. Collection of Brønsted-type correlations

Equilibria

$$ArNHCSOC_6H_4\text{-}4\text{-}OMe \rightleftharpoons ArN\overset{-}{C}SOC_6H_4\text{-}4\text{-}OMe + H^+$$
$$pK^{NH} = 0.62\ pK^{ArNH_3+} + 6.33\ (r\ 0.995)$$

$$PhNHCSOAr \rightleftharpoons PhN\overset{-}{C}SOAr + H^+$$
$$pK^{NH} = 0.72\ pK^{ArOH} + 1.80\ (r\ 0.900)$$

$$3\text{-}NO_2C_6H_4NCS + Ar\overset{-}{O} \rightleftharpoons 3\text{-}NO_2C_6H_4N\overset{-}{C}SOAr$$
$$\log K_{eq} = 1.95\ pK^{ArOH} - 18.31\ (r\ 0.944)$$

Rates

$$ArN\overset{-}{C}SOC_6H_4\text{-}4\text{-}OMe \xrightarrow{k_1} ArNCS + \overset{-}{O}C_6H_4\text{-}4\text{-}OMe$$
$$\log k_1 = 0.26\ pK^{ArN_3H+} - 2.58\ (r\ 0.994)$$

$$ArNCS + PhO^- \xrightarrow{k_{-1}} ArN\overset{-}{C}S\text{-}OPh$$
$$\log k_{-1} = -0.27\ pK^{ArNH_3+} - 0.026\ (r\ 0.996)$$

$$PhN\overset{-}{C}SOAr \xrightarrow{k_1} PhNCS + \overset{-}{O}Ar$$
$$\log k_1 = -0.91\ pK^{ArOH} + 7.83\ (r\ 0.997)$$

$$3NO_2C_6H_4N\overset{-}{C}SOAr \xrightarrow{k_1} 3NO_2C_6H_4NCS + \overset{-}{O}Ar$$
$$\log k_1 = -1.28\ pK^{ArOH} + 11.03\ (r\ 0.93)$$

$$3NO_2C_6H_4NCS + \overset{-}{O}Ar \xrightarrow{k_{-1}} 3NO_2C_6H_4N\overset{-}{C}SOAr$$
$$\log k_{-1} = 0.81\ pK^{ArOH} - 8.72\ (r\ 0.948)$$

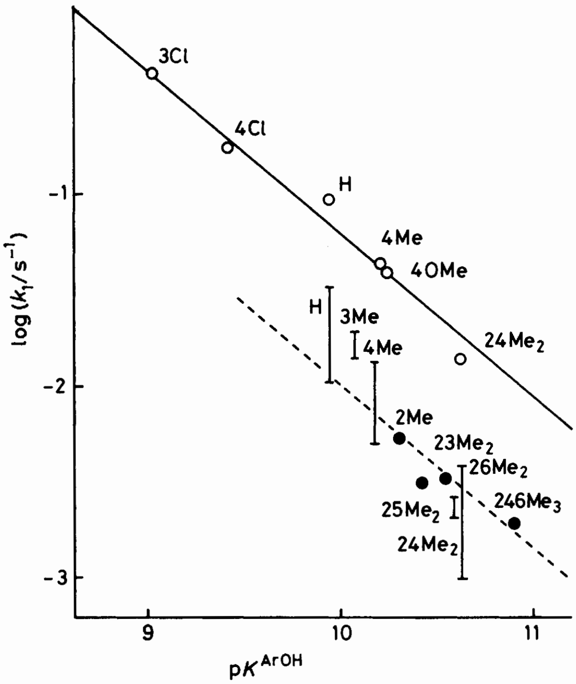


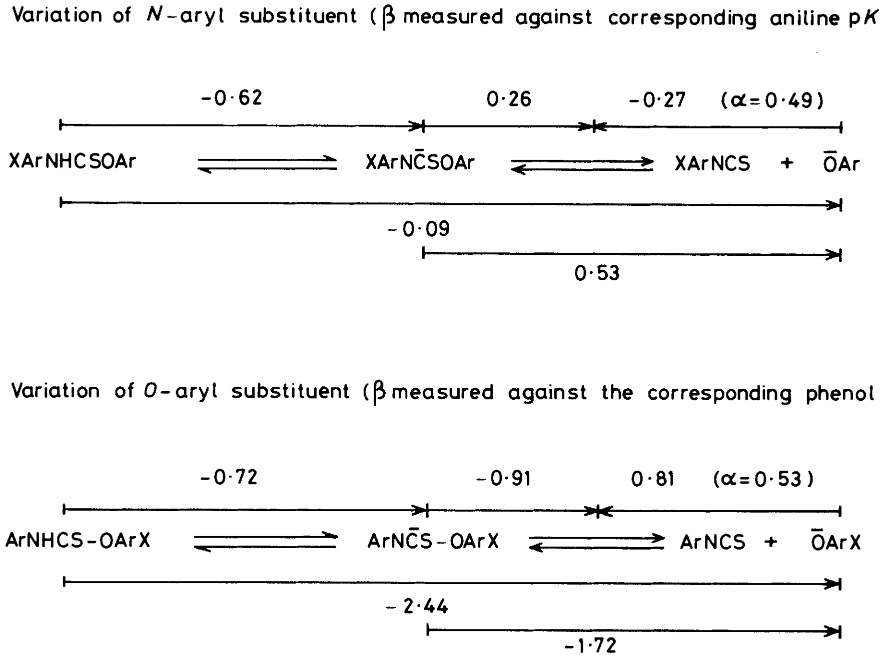
Figure 5. Brønsted type correlations *versus* pK of the leaving phenol of the decomposition of the conjugate anion of the thioncarbamate: filled circles, *N*-3-nitrophenylthioncarbamate (Table 5); open circles, *N*-phenylthioncarbamate (Table 3). The full line is theoretical from parameters in Table 6; the broken line is arbitrary with a slope equal to that of the full line

Ph]/[PhO$^-$][4-NO$_2$C$_6$H$_4$NCS] > 23), comparing favourably with the observed value of 0.66.

Variation of Substituents in the N-*Aryl Group.*—The rate and ionisation parameters for the degradation of *O*-4-methoxyphenyl *N*-arylthioncarbamates were measured and the results are collected in Table 2 together with the hydrolysis rate parameters of isothiocyanates. A Hammett σ correlation is observed for k_1; the data for this plot include the rate constants determined directly from thioncarbamate hydrolysis and the 4-nitrophenyl parameter from data from synthetic rate experiments. In the latter case we were not able to synthesise the ester preparatively so we did not obtain the pK for this species. Attack of phenolate ion on substituted isothiocyanates (Table 3) has a simple Brønsted type dependence on the pK of the corresponding aniline (Table 6).

Variation of Substituents in the Phenol Leaving Group.—Calmon and his co-workers[6] studied the degradation of *O*-aryl *N*-phenylthioncarbamates and dissected the rate parameter for the decomposition of the conjugate anion from the ionisation element. We have extended this work utilising a fast mixing apparatus; the ionisation constant and decomposition rate constant (k_1) obey good Brønsted relationships against the pK of the corresponding phenol (Table 6) and the data are recorded in Table 4.

The synthesis of thioncarbamates from aryloxide and isothiocyanate was followed as described for the 4-nitrophenyl isothiocyanate but the most convenient isothiocyanate for study proved to be the 3-nitro-derivative. As described earlier the method gives both synthetic (k_{-1}) and degradative (k_1) rate

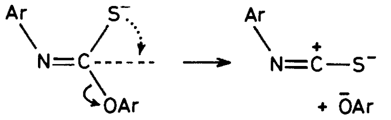


Scheme 1. Values of Brønsted β for rates and equilibria for degradation of *N*-aryl *O*-arylthioncarbamates

parameters; since this reaction is followed at a pH well above the p*K* of *O*-aryl *N*-3-nitrophenylthioncarbamate the degradation rate constant for the conjugate anion is derived directly (Table 5). The uncertainties in measuring k_1 are such that the Brønsted dependence is not of the best reliability for this reaction. Figure 5 illustrates that the Brønsted slope (with a relatively good correlation coefficient) for the decay of PhN$\bar{\text{C}}$SOAr could be encompassed by the results for the *N*-3-nitrophenyl analogues and we assume this slope to be valid for the latter reactions. The data for the synthesis which is derived from the slope of the rate constant *versus* phenolate ion concentration is better than the degradative data except that the least reactive phenolate ions have considerable uncertainty due to the relatively small changes observed in the ' raw ' rate constant data for these nucleophiles.

Discussion

Substituent Effects on Reactivity.—Variation of the *N*-aryl substituent has little effect on the decomposition of the conjugate base (β 0.26) and the Hammett σ correlation of k_1 indicates little change in resonance interaction from anion to transition state. Perusal of Scheme 1 indicates that the C–O bond undergoes substantial alteration as measured by the effect of substituents on the leaving phenol and of course this bond is completely cleaved in the reaction. We conclude that the main bonding changes during decomposition are an alteration of NCS bond angle, cleavage of C–O and increase of positive charge on carbon [equation (7)]. The stereochemistry of the cleavage reaction will involve all the major atoms of the system being essentially planar. Departure of $\bar{\text{O}}$Ar perpendicular to the ArNC plane will involve the NC bond in considerable bond change during the reaction contrary to the effect of substituents on the *N*-aryl function. The $\bar{\text{O}}$Ar group must depart *trans* to the ArN moiety as the reverse reaction, addition of ArO^- to isothiocyanate, is sterically hindered for the *cis*-path. Addition of the ArO^- group to isothiocyanate is thus ' across ' the π (formal) C=S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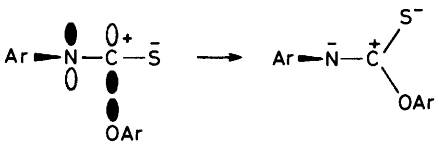
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bond and not ' across ' the N=C π bond system. Addition of ArO^- across the C=N bond [equation (8)] would give initially a ' skewed ' thioncarbamate system which is certainly less stable than the planar one proposed but would also cause significant negative charge increase on the nitrogen giving a much larger negative β value than the observed one (−0.27, see Scheme 1) and also a Hammett σ^- dependence for k_1.

Cycloaddition to isocyanates occurs predominantly across the NC double bond whereas isothiocyanates have a tendency to add across the CS bond; [12] these results are for the isolated product. It is probable that initial addition occurs ' across ' the C=O π bond in the isocyanate case for the same reason as for CS addition in isothiocyanates, namely that a skewed amide intermediate would otherwise be formed. Certainly the use of the C=O π orbitals in the initial step of a stepwise cycloaddition to the isocyanate do not preclude the regioselectivity found in the final product.

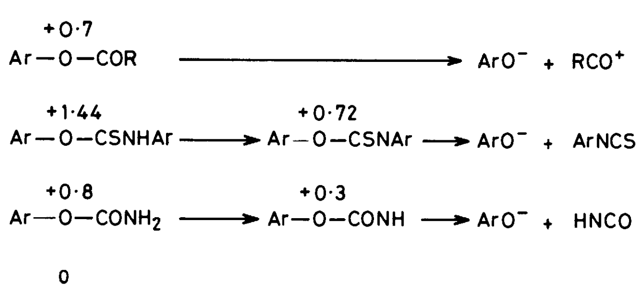
Substituent Effects on Equilibria.—The Brønsted-type parameters measured against the ionisation of the substituted phenol or aniline as standard equilibria are set out in Scheme 1. It should be appreciated that except where equilibria have been explicitly measured the forward and reverse β values are not necessarily for the same substrate. Reference to Table 6 identifies the experimental values. We can assume that the

Table 7. Equilibrium constants for addition of nucleophiles to heterocumulenes in aqueous solution

Equilibrium	K/l mol^{-1} [t]	K'/l mol^{-1} [t]
$HNCO + HOPh \rightleftharpoons NH_2COOPh$	1.07×10^4 [b]	0.076 [a]
$HNCO + HSPh \rightleftharpoons NH_2COSPh$	1.4×10^5 [e]	4.5×10^{-4} [f]
$HNCO + NH_3 \rightleftharpoons NH_2CONH_2$	1.1×10^{11} [c]	1.1×10^{-3} [c]
$OCO + HOPh \rightleftharpoons HOCOOPh$	7.77×10^{-10} [d]	1.32 [d]
$OCO + Bu^nNH_2 \rightleftharpoons HOCONHBu^n$	0.73 [g]	2.5×10^{-2} [i]
$SCS + MeNH_2 \rightleftharpoons HSCSNHMe$	4.7×10^3 [j]	$<4.7 \times 10^3$ [k]
$OCS + Bu^nNH_2 \rightleftharpoons HOCSNHBu^n$	0.092 [l]	6.5×10^{-4} [m]
$PhNCO + HCl \rightleftharpoons PhNHCOCl$	1.6×10^2 [n]	
$PhNCS + HOPh \rightleftharpoons PhNHCSOPh$	0.05 [p]	0.42 [p]
$PhNCS + Pr^nSH \rightleftharpoons PhNHCSSPr^n$	9.7×10^6 [q]	3.0×10^5 [q]
$RNCNR + HOPh \rightleftharpoons RHNC(NR)OPh$	$>1.8 \times 10^4$ [r]	$>3.2 \times 10^{-4}$ [s]

[a] Data from Table III in ref. 16. [b] $[NH_2COOPh]/[HOPh][HNCO] = [\overset{-}{N}HCOOPh]K^{PhOH}/[Ph\overset{-}{O}][HNCO]K^{NH} = K'K^{PhOH}/K^{NH}$; $K^{PhOH} = 10^{-9.95}$, $K^{NH} = 10^{-15.1}$ (see Table V of ref. 16). [c] A. Williams and W. P. Jencks, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1760. [d] Calculated from a Brønsted plot for alcohols in C. K. Sauers, W. P. Jencks, and S. Groh, *J. Am. Chem. Soc.*, 1975, **96**, 5546; pK^{PhOCO_2H} calculated using $pK^{RCO_2H} = 4.66 - 1.62\sigma^*$ and $\sigma^* = 2.43$ (G. B. Barlin and D. D. Perrin, *Quart. Rev. Chem. Soc.*, 1966, **20**, 75. [e] N. Bourne and A. Williams, unpublished observation $[PhSCONH_2][OH^-]/[PhS^-]/[HNCO] = 5.7 \times 10^{-3}$. [f] $[PhSCONH]K_w/K^{NH}[PhS^-][HNCO] = 5.7 \times 10^{-3}$; $pK^{NH} \approx 15.1$ [2] $pK^{PhSH} = 6.62$ (P. de Maria, A. Fini, and F. M. Hall, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1969. [g] The p*K* of Bu^nNHCO_2H is calculated as in footnote *d* to be 3.66 (σ^* is taken as 0.62); $[Bu^nNHCO_2^-][H]/[CO_2][Bu^nNH_2] = 0.48 \times 10^3/4.7 \times 10^7$; data from M. B. Jensen, *Acta Chem. Scand.*, 1957, **11**, 499; S. P. Ewing, D. Lockshon, and W. P. Jencks, *J. Am. Chem. Soc.*, 1980, **102**, 3072. [i] The p*K* of $Bu^n\overset{+}{N}H_2\overset{-}{CO_2}$ is calculated from the relationship $pK^{R\overset{+}{N}H_2\overset{-}{CO_2}} = pK^{RNH_3} - 8.4$ found in Ewing *et al.* (reference in footnote *g*). [j] $[MeNHCS_2H]/[CS_2][MeNH_2] = 1.66/3.5 \times 10^{-4}$; data from P. J. Kothari and M. M. Sharma, *Chem. Eng. Sci.*, 1966, **21**, 391; S. J. Joris, K. I. Aspila, and C. L. Chakrabarti, *J. Phys. Chem.*, 1970, **74**, 860. [k] The p*K* of $MeNHCS_2H$ taken from D. M. Miller and R. A. Latimer, *Can. J. Chem.*, 1962, **40**, 246; the p*K* of $Me\overset{+}{N}H_2\overset{-}{CS_2}$ is less than that of the neutral acid but the value is not known thus: $[Me\overset{+}{N}H_2CS_2]/[CS_2][MeNH_2] = 4.7 \times 10^3$; $K^{MeNHCS_2H}/K^{Me\overset{+}{N}H_2CS_2} < 4.7 \times 10^3$. [l] $[Bu^nNHCOS^-][H]/[COS][Bu^nNH_2] = 1.14/3.5 \times 10^4$; data from Kothari and Sharma (footnote *j*) and Ewing *et al.* (footnote *g*). The p*K* of $Bu^nNHCOSH$ is taken as $pK^{MeNHCS_2H} + 0.56$ because $pK^{PhCOSH} = pK^{PhCS_2H} + 0.56$. [m] The p*K* of $Bu^n\overset{+}{N}H_2\overset{-}{COS}$ is estimated from the equation $pK^{R\overset{+}{N}H_2\overset{-}{COS}} = pK^{RNH_3} - 11.9$ (Ewing *et al.* in footnote *g*) $[Bu^n\overset{+}{N}H_2\overset{-}{COS}]/[COS][Bu^nNH_2] = 1.14/3.5 \times 10^4$. $K^{Bu^n\overset{+}{N}H_2\overset{-}{COS}} = 1.14/3.5 \times 10^4 \times 10^{-1.3}$. [n] Data for acetonitrile at 25° from R. Bacaloglu and C. A. Bunton, *Tetrahedron*, 1973, **29**, 2721. [p] This work, $[PhNHCSOPh]/[PhOH][PhNCS] = 0.044 \times 10^{-9.95}/1.04 \times 10^{-1} \times 10^{-9.04}$; data for pK^{NH} and decomposition of PhNHCSOPh from Table 4; reaction of $Ph\overset{-}{O}$ with PhNCS calculated from the correlation in Table 6. [q] $[Ph\overset{-}{N}CSSPr^n]/[PhNCS][Pr^nS^-] = 773/2.55 \times 10^{-3}$; $[PhNHCSSPr^n]/[PhNCS][Pr^nSH] = 3.0 \times 10^5 K^{NH}/K^{SH}$; data from L. Drobnica and P. Gemeiner, *Collect. Czech. Chem. Commun.*, 1975, **40**, 3346; $pK^{Pr^nSH} = 10.62$ (M. M. Kreevoy, E. T. Harper, R. E. Duvall, H. Wilgus, and L. T. Ditsch, *J. Am. Chem. Soc.*, 1960, **88**, 4899). [r] Decomposition of RNHC(NR)OPh in the presence of hydroxide ion gives the rearranged product RNHCONRPh; the rate constant thus gives us an upper limit for the return reaction to carbodi-imide and phenolate anion. This rate constant has been used to calculate a lower limit for *K* and *K'*. [s] The p*K* of the *O*-phenyl isomer is 17.7 (I. T. Ibrahim and A. Williams, *J. Chem. Soc., Perkin Trans, 2*, 1982, 1459). [t] *K'* is the equilibrium constant for formation of initial adduct from reactants (see text). The overall equilibrium constant to neutral products is *K*.

choice of substrate has little effect on the magnitude of the β value and this assumption is probably quite valid as there is only a very small change in reactivity and structural type.[13,14]



Scheme 2. Numbers refer to the 'effective' charge on the ether oxygen

The effect on the equilibrium of varying substituents on the phenol leaving group is much larger than that on equilibria for ordinary acyl group transfer reactions[15] (Scheme 2) where the 'effective' charge * on the ether oxygen of the ester is +0.7 relative to a unit change in 'effective' charge on the oxygen in the standard phenol ionisation equilibrium. The conjugate base has less 'effective' charge on the oxygen than in the neutral species as expected and as found for the corresponding carbamate series.[15,16] The very high positive 'effective' charge on the ether oxygen of thioncarbamates indicates essentially that the ArNHCS function is more electropositive than either the hydrogen substituent (H) or the regular acyl or carbamoyl functions (RCO or RNHCO). The data are also consistent with $Ar\overset{-}{N}CS$ being more electropositive than H and of similar polarity to the acyl group. We interpret thse results in terms of the known $\overset{+}{C}-\overset{-}{S}$ character of the thione 'double' bond resulting from the relatively weak π-bonding energy compared with that of the carbonyl function. There is a difference of *ca.* 40 kcal mol^{-1} between the π-bond energy of CS and CO double bonds.[17] Presumably anti-bonding interactions contribute to the low efficiency of 2*p*–3*p* π-overlap in C=S compared with 2*p*–2*p* in C=O. Comparison of dipole moments of C=S and C=O compounds[18] provides further evidence for the $\overset{:+}{C}-\overset{-}{S}$ (Scheme 3) character of thiones and we conclude that the resonance structures bearing positive nitrogen or carbon are more important than the corresponding ones of the carbamate. The p*K* values of thion-

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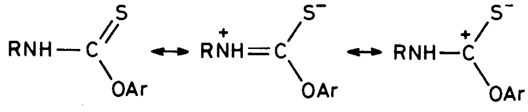
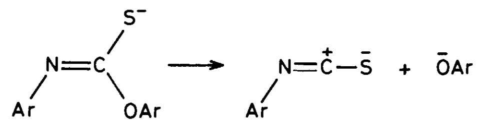
* 'Effective' charge has a purely operational significance and is defined in ref. 15.



Scheme 3

amides and the present thioncarbamates are significantly lower than those of the corresponding oxygen analogue [19a] consistent with the importance of the dipolar structures. The effect of substituent change in the OAr function on the ionisation is approximately the same as that (β 0.5) calculated from Hegarty's work for aryl *N*-4-nitrophenylcarbamates.[19b] Comparison of ' effective ' charges with those determined by MO theory (CNDO) [20] indicates that the experimental values are too positive. There are no data available for thioncarbamates but methanol, formamide, and formic acid [21] have -0.247, -0.237, and -0.256 electron units on the oxygen, nitrogen, and ether oxygen respectively; the ' effective ' charges on the corresponding atoms in similar compounds determined from substituent effects are 0, $+0.7$, and $+0.7$, respectively.[15] The difference between the theoretical and estimated values is probably due to extensive solvation as the former are for the gas phase and the latter for aqueous solvent.

The effects of variation of the *N*-aryl substituent on equilibrium and rate parameters are correlated with the p*K* of the corresponding anilinium ion (Scheme 1). The ionisation has a sensitivity of -0.62 indicating a significant change in charge on the nitrogen relative to that in the standard equilibrium. This is consistent with the conclusion that the zwitterion canonical with the ground state (Scheme 3) is a major contributor; the conclusion is strengthened by the argument that ionisation of neutral anilines also has a Brønsted sensitivity of *ca.* -0.6.[21] The equilibrium constant for formation of isothiocyanate from the conjugate base has a sensitivity to *N*-aryl substituents of $+0.53$ relative to the aniline ionisation. We believe that this sensitivity is consistent with a structure of reactant and product states involving little change in charge on the nitrogen [equilibrium (9)]. It is difficult for the substituent to interact with the negative charge on the sulphur in the reactant because of the very poor $2p$–$3p$ π-bonding overlap between carbon and sulphur. The $\mathrm{Ar\overset{+}{N}{\equiv}\overset{-}{C}{-}\overset{-}{S}}$ structure is not a contributor to the isothiocyanate resonance hybrid as the ArNC bond angle is known to be much less than 180°.* The *N*-aryl substituent cannot interact by resonance with the positive carbon in the isothiocyanate as the symmetry of the orbital on this carbon is not compatible with the π-orbitals of the aromatic ring. The overall change in charge ' seen ' by the *N*-aryl substituent is thus relatively small, consistent with the present result.



(9)

Transition-state Index.—Many studies have been made of reactions using Brønsted β values as measures of transition-state structure and most of these can only be regarded as interim because the standard reaction against which β is measured is usually very different (usually an ionisation) from the reaction in hand. The reason for the paucity of data of the Leffler type is that it is usually easy to measure a reaction rate in one direction but not in both. The use and meaning of Brønsted parameters with respect to the structure of the transition-state has received considerable theoretical discussion [23] but the lack of data on substituent effects on rate constants against those on the equilibrium for the reaction hampers an experimental approach to the problem.

The effect of substituent change in the *N*-aryl group on the reacting bond (C–OAr) is fed through a different interaction path from that of the substituent change in the *O*-aryl group. The values of α for these two different paths are 0.49 and 0.53, respectively, and are identical within the experimental limits. That this identity is significant is confirmed by the gross dissimilarity of the β_{EQ} values (0.53 and -1.72, respectively, for *N*- and *O*-aryl substituents). We conclude that the Leffler assumption holds for this simple addition reaction. This result is consistent with expectation as the reaction is essentially a simple process involving major bond changes at a single bond centre namely the C–O bond. We can deduce from the figures in Scheme 1 that the transition state behaves as if it were *ca.* 50% between ground and product states. We must emphasise that this conclusion refers to the ground, transition, and product state systems which naturally include solvent interaction.

Previous authors [24] including ourselves [15,25] have studied multiple structure interactions for reactions involving major changes at *two bond* centres. The α parameters obtained for these bonds are not required to be identical and any imbalance is useful information regarding the timing of bond cleavage provided the Leffler assumption holds for each centre.

Concerted versus *Stepwise Addition.*—The addition of aryloxide ion to isothiocyanate yields an anionic species of low p*K*. It is not possible to estimate the p*K* of the conjugate acid of the isothiocyanate (*N*-protonated) although this must certainly be less than zero; it is probably lower than that of the correponding isocyanate owing to the stronger contribution to the isothiocyanate structure of $\mathrm{RN{=}\overset{+}{C}{-}\overset{-}{S}}$ compared with $\mathrm{RN{=}\overset{+}{C}{-}\overset{-}{O}}$ in the isocyanate. *N*-Protonated isothiocyanates have been prepared but in non-nucleophilic solvents.[26] Assuming the catalytic acid has a p*K* of 7 then the various free energy levels are obtained as illustrated in Figure 6. The analogous attack of phenoxide ion on isocyanic acid in the presence of an acid of p*K* 7 leads to a product which is more favoured relative to the reactant but the anion is less stable for the oxygen analogue; the free energy surface is markedly skewed favouring the stepwise addition to the heterocumulenes in agreement with the experimental conclusions. Amine attack on isothiocyanates should also possess a skewed diagram favouring the zwitterionic intermediate and there is no evidence of general buffer catalysis consistent with a concerted process.[27]

Equilibrium Constants for Addition to Heterocumulenes.—The ability of sulphur or oxygen to stabilise a negative charge in the adducts of phenolate ion with isocyanate, isothiocyanate, and carbon dioxide probably accounts for the equilibrium series (K') HNCO < PhNCS < CO_2. The overall equilibrium constants (K) for this set of reactions are in the order $CO_2 \ll$ PhNCS $\ll$ HNCO $\lesssim$ RNCNR; the alteration in the

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* Early work [22a] considered the $\mathrm{R\overset{+}{N}{\equiv}C{-}S}$ canonical as being the major contributor to the isothiocyanate structure but this is not able to take into account the ArNC bond angle. It is surprising that quite recent work [22b] has favoured the above structure as a contributor together with $\mathrm{ArN{=}\overset{+}{C}{-}\overset{-}{S}}$ despite the gross geometrical differences between the canonical forms.

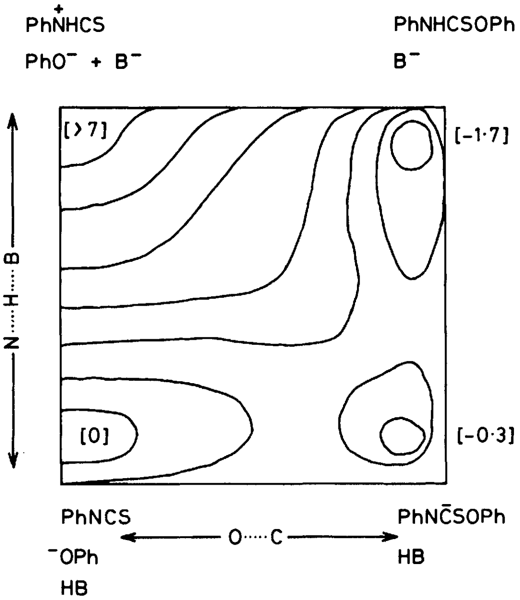

Figure 6. Contour diagram for the reaction of phenyl isothiocyanate with phenolate ion in the presence of acid (HB) of p*K* 7. The figures in parenthesis refer to $-\log K$ for the equilibrium constants referred to formation from isothiocyanate (see text). The equilibrium constants are theoretical derived from data in Tables 4 and 6

Table 8. Reactivity and sensitivity for reaction of nucleophiles with some heterocumulenes in aqueous solution

Hetero-cumulene	Nucleo-phile	k_{-1}/l mol^{-1} s^{-1}	β_{nuc}	TS1
HNCO	ArO^-	210 [16,b]	0.66 [16]	0.5
HNCO	R_3N	1 300 [27,c]	0.3 [27]	
PhNCS	ArO^-	5.3×10^{-2} [d]	0.81 [f]	0.49
EtNCS	R_3N	4.2×10^{-2} [c]	0.28 [27]	
CO_2	RO^-	3 600 [b,c]	0.3 [e]	0.21 [e]
CO_2	R_3N	4 300 [c,g]	0.26 [g]	
CS_2	R_3N	0.013 [c,h]	0.26 [h]	
COS	R_3N	13 [c,h]	0.26 [h]	
RNCNR	R_3N	1.5×10^{-2} [a]	0.3 [a]	

[a] $EtNCNCH_2CH_2CH_2NMe_3^+$ against ethylamine, I. T. Ibrahim, unpublished work. [b] Nucleophile for comparison is PhO^-. [c] Nucleophile is methylamine. [d] Calculated from equation in Table 6. [e] Calculated from C. K. Sauers, W. P. Jencks, and S. Groh, *J. Am. Chem. Soc.*, 1975, **96**, 5546. [f] This work. [g] M. B. Jensen, *Acta Chem. Scand.*, 1959, **13**, 289. [h] M. M. Sharma, *Trans. Faraday Soc.*, 1965, **61**, 681.

order of these constants is due to the proton transfer equilibria *after* the initial adduct formation. The *O*-phenylisourea from the carbodi-imide is especially stable due to the very favourable proton transfer. The lack of driving force in the proton transfer from the carbon dioxide case is sufficient to make this overall equilibrium constant highly unfavourable. It is interesting that the reactivity (Table 8) of the phenolate ion towards the heterocumulene roughly parallels the equilibrium constant for formation of the initial adduct where this is known.

The equilibrium constants for formation of the initial *adduct* from amines and heterocumulenes are in the order COS < CO_2 < CS_2 < HNCO. The *overall* equilibrium constant is more favourable than that for zwitterion formation although the extent is uncertain for CS_2. The effect of the sulphur is to increase the equilibrium constant for formation but where data are available the reactivity to amines is in the order CO_2 > HNCO > COS > CS_2 and bears no relationship to the magnitude of *K'*.

Perusal of Table 7 reveals that the equilibrium constants for overall formation of products from thiol attack are generally large. The low value of *K'* for attack of thiophenoxide on isocyanic acid may be due to the stability of the thiophenoxide group. Reference to Scheme 1 indicates that the formation of thioncarbamate is favoured by the more basic phenolate anions. Presumably the same sensitivity holds for dithiocarbamates from thiophenols and we believe this acidity difference explains the more favourable equilibrium constant for formation of dithiocarbamates from alkanethiols compared with that for thiocarbamates from thiophenol.

The quantitative equilibrium constants determined in this study confirm the synthetic observations that phenyl thioncarbamates are not obtained in good yield from isothiocyanates whereas alkyl esters are.[28] The data of Scheme 1 and Table 7 indicate that the equilibrium constant will become favourable as the acidity of the hydroxy function is reduced. The substituents on the nitrogen have little effect on the equilibrium constants and hence presumably on the synthetic utility of the isothiocyanate. Formation of dithiocarbamates from isothiocyanates is synthetically useful in agreement with the favourable equilibrium constant. Thioureas are produced in high yield from aqueous solution presumably because of the favourable proton transfer reactions following zwitterion formation. It is noted that most of the overall equilibrium constants quoted in Table 7 are favourable in accord with the known synthetic utility of these reactions.

Note added in proof: Professor E. S. Lewis (C. D. Ritchie, J. D. Saltiel, and E. S. Lewis, *J. Am. Chem. Soc.*, 1961, **83**, 4601) has brought to our attention that the Leffler–Grunwald parameters from two interactions are also identical for a simple N–S bond fission.

Acknowledgements

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