The Stabilities of Meisenheimer Complexes. Part XIII.[1] Kinetic and Equilibrium Data for Spiro-complex Formation from 1-(2-Mercaptoethylthio)- and 1-(2-Hydroxyethylthio)-2,4,6-trinitrobenzene in Water

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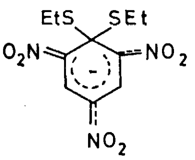
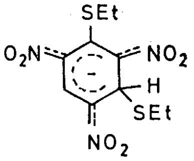
Cyclisation of 1-(2-mercaptoethylthio)-2,4,6-trinitrobenzene occurs in water to give a spiro complex (III), of high thermodynamic stability. Opening of the dithiolan ring of (III) is catalysed by mercury(II) ions but not by acids. In the presence of aqueous base cyclisation of 1-(2-hydroxyethylthio)-2,4,6-trinitrobenzene to the spiro complex (IV) is followed by irreversible decomposition to ethylene sulphide and picrate ions. Kinetic and equilibrium data for the formation of (III) and (IV) are reported and are compared with those for the analogous dioxolan, complex (V).

MUCH kinetic and equilibrium data is now available relating to the formation of Meisenheimer complexes [2] and spiro-complexes [3,4] from nitro-activated substrates and oxygen bases. The information regarding the formation of analogous σ-complexes from thiolate ions is in most cases less quantitative although values of the equilibrium constants for the addition of sodium ethane- and benzene-thiolate to 1,3,5-trinitrobenzene and some nitroanilines have been reported.[5] In these cases addition occurs at unsubstituted ring positions. Pietra and Biggi [6] studied the reaction of sodium ethanethiolate with ethyl thiopicrate and found n.m.r. evidence for the formation of two products, (I) and (II). Both isomers were present at equilibrium with the 1,3-adduct, (II), predominating. This is in marked contrast to the analogous reactions of oxygen bases with alkyl picrates where addition at the 3-position is kinetically preferred but addition at the 1-position gives the thermodynamically more stable product.[2]



(I)



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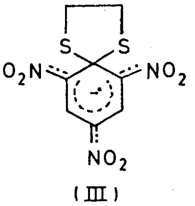
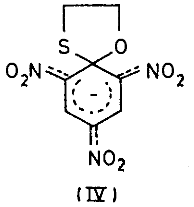


(III)



(IV)

Preparations of the spiro-complexes (III),[7,8] as a stable compound, and (IV), [8,9] as an intermediate, have recently been reported. Kinetic and equilibrium data relating to these complexes are now reported.

EXPERIMENTAL

^1H N.m.r. spectra were measured with a Bruker HX90 instrument, using tetramethylsilane as internal reference. U.v.–visible measurements were made with Unicam SP 8000 and SP 500 instruments and with a Canterbury stopped-flow spectrophotometer.[3] Solutions of suitable concentration were prepared immediately before use from freshly made stock solutions of reagents.

The spiro-complex (III) was prepared as the potassium salt from picryl chloride and ethane-1,2-dithiol by the method of Pietra *et al.*[7] The ^1H n.m.r. spectrum in $[^2H_6]$DMSO showed two singlets at δ 8.33 and 3.86 attributed respectively to the ring and methylene protons. The visible spectrum was similar to that previously reported [8] showing maxima in water at 458 (ε 1.8×10^4 l mol^{-1} cm^{-1}) and 550 nm (7.7×10^3), and in methanol at

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[1] Part XII, M. R. Crampton and M. J. Willison, *J.C.S. Perkin II*, 1976, 160.

[2] M. R. Crampton, *Adv. Phys. Org. Chem.*, 1969, **7**, 211; M. J. Strauss, *Chem. Rev.*, 1970, **70**, 667.

[3] M. R. Crampton and M. J. Willison, *J.C.S. Perkin II*, 1974, 1681 and references therein.

[4] C. F. Bernasconi and H. S. Cross, *J. Org. Chem.*, 1974, **39**, 1054.

[5] M. R. Crampton, *J. Chem. Soc.* (*B*), 1968, 1208; 1971, 2112.

[6] G. Biggi and F. Pietra, *J.C.S. Perkin I*, 1973, 1980.

[7] E. Farina, C. A. Veracini, and F. Pietra, *J.C.S. Chem. Comm.*, 1974, 672.

[8] V. N. Knyazev, A. A. Klimov, N. G. Yaryshev, and V. N. Drozd, *Zhur. org. Khim.*, 1974, **10**, 2587.

[9] C. C. Culvenor, W. Davies, and W. E. Savige, *J. Chem. Soc.*, 1952, 4480.

450 (ε 2.1×10^4 l mol^{-1} cm^{-1}) and 540 nm (8.8×10^3). Measurements were made in methanol containing various concentrations of methoxide ions. No change in spectral shape or optical density (<1%) was found in the following solutions: (*a*) AnalaR methanol; (*b*) *p*-bromophenol–*p*-bromophenolate buffer with residual methoxide concentration of 1.0×10^{-4}M; (*c*) 10^{-2}M-sodium methoxide.

1-(2-Hydroxyethylthio)-2,4,6-trinitrobenzene was prepared as before[9] by the reaction of picryl chloride and 2-mercaptoethanol in ethanol containing sodium acetate. Recrystallisation from benzene gave a yellow material, m.p. 72° (lit.,[9] 72°), δ ([$^2H_6$]DMSO) 9.14 (s, ring protons), 3.6 (t, *J* 6 Hz, β-CH_2), 3.05 (t, *J* 6 Hz, α-CH_2), and 3.6br (OH). The addition of sodium deuterioxide in deuterium oxide caused the solution in DMSO to turn deep red. New bands attributable to the spiro-complex (IV) were observed at δ 8.47 (s, ring protons), 4.62 (m, OCH_2), and 3.58 (m, SCH_2). With time these bands decreased in intensity and new bands at δ 8.71 (s) and 2.47 (s), grew at their expense. These latter bands can be attributed to the decomposition products, the picrate ion and ethylene sulphide respectively.

optical densities at 458 nm were made in buffered solutions in the pH range 4—8 and are given in Table 1.

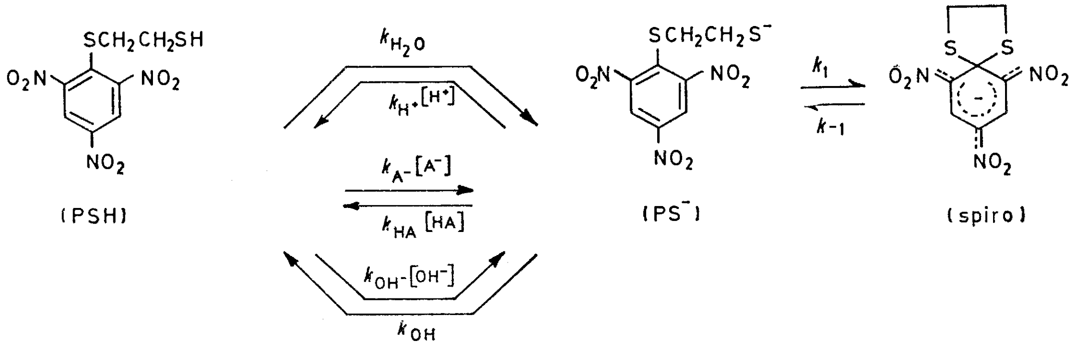
TABLE 1

Equilibrium data for formation of complex (III) from 1-(2-mercaptoethylthio)-2,4,6-trinitrobenzene in aqueous buffers at 25°

pH	Conditions	O.D.$_{458}$[a]	$10^{-8}K_c$
4.22	*b*	0.098	9.5
4.65	*b*	0.225	10
5.15	*b*	0.426	10
5.65	*b*	0.583	9.5
6.10	*c*	0.653	8
6.63	*c*	0.710	
7.20	*c*	0.715	
7.60	*c*	0.720	

[a] Measured with Unicam SP 500 with 4.0×10^{-5} M substrate. [b] Phthalate buffer, 0.05M. [c] Phosphate buffer, 0.05M.

The only species carrying a delocalised negative charge and hence likely to absorb at this wavelength is the spiro-complex. Hence these measurements give the extent of conversion of PSH and PS$^-$ to spiro-complex.



SCHEME 1

1-(2-Hydroxyethylthio)-2,4-dinitrobenzene was prepared by the reaction of 1-chloro-2,4-dinitrobenzene with 2-mercaptoethanol in ethanol containing sodium acetate. Recrystallisation from benzene yielded yellow needles, m.p. 102° (lit.,[9] 100°), δ ([$^2H_6$]DMSO) 8.93 (d, H-3), 8.50 (dd, H-5), 8.00 (d, H-6), 3.3 (t, *J* 6 Hz, α-CH_2), 3.8 (q, *J* 6 Hz, β-CH_2), and 5.2 (t, *J* 6 Hz, hydroxy). The addition of sodium deuterioxide in deuterium oxide resulted in the fast formation of ethylene sulphide, δ 2.47 (s), and 2,4-dinitrophenolate ions, δ 8.72 (d, H-3), 7.94 (dd, H-5), and 6.48 (d, H-6).

RESULTS AND DISCUSSION

1-(2-*Mercaptoethylthio*)-2,4,6-*trinitrobenzene*.— The spiro-complex (III) derived from the parent thiol dissolves in water to give a red solution with $\lambda_{max.}$ 458 (ε 1.8×10^4 l mol^{-1} cm^{-1}) and 550 (7.7×10^3). The similarity of the visible spectrum to that for the spiro-complex in DMSO,[7] where there is ^{1}H n.m.r. evidence for structure (III), argues strongly that no unwanted structural change occurs on solution of the complex in water. There is a very slow irreversible decomposition reaction yielding unidentified products.

One pathway for interconversion of the parent (PSH) and spiro-complex will involve the parent anion (PS$^-$) as shown in Scheme 1. Measurements of the equilibrium

As before[3] the measured equilibrium constant K_c is related by equation (1) to the equilibrium constant

$$K_c = KK_1/(1 + K[HO^-]) \qquad (1)$$

K (= [PS$^-$]/[PSH][HO$^-$]), governing transfer of the side-chain proton to hydroxide ions, and the equilibrium constant K_1 governing internal cyclisation. We note that since K is simply related to the acid dissociation constant, K_a, of PSH ($K = K_a/K_w$, where K_w is the autoprotolysis constant of water) an alternative form of equation (1) may be written in terms of K_a and [H$^+$]. The value of the acid dissociation constant of PSH is not known. However the pK_a values for ethanethiol and 2-ethoxyethanethiol are 10.6 and 9.4 respectively.[10] We would, then, expect the pK_a value for PSH to be in the range 10 ± 1, so that the value of K is likely to be near 10^4 l mol^{-1}. Therefore under the conditions used in the present work $K[OH^-] \ll 1$ so that the denominator of equation (1) will approximate to unity. The data in Table 1 give a value for K_c, and hence for KK_1, of $(1 \pm 0.3) \times 10^9$ l mol^{-1}. For comparison Drozd *et al.*[8] report that in 50% aqueous ethanol conversion to complex is half-complete in a solution of apparent pH

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[10] M. R. Crampton, 'The Chemistry of the Thiol Group,' Wiley–Interscience, London, 1974, p. 398.

3.67. They also report a value for K_c in methanol of 2.5×10^3 l mol^{-1}. This latter value seems surprisingly small in view of our previous measurements[3] which indicate that values for equilibrium constants for spiro-complex formation in water and methanol do not differ greatly. We think that their value in methanol is unreliable probably because the solvent contained traces of acidic impurities, such as carbon dioxide. Our measurements (Experimental section) indicate $>99\%$ conversion to complex in neutral methanol indicating a much higher value for K_c.

The kinetics of the interconversion of PSH and spiro-complex were studied by stopped-flow spectrophotometry. Solutions of the spiro-complex in water were mixed with solutions containing hydrochloric acid or acidic buffers and the decrease with time of visible absorption measured. Since the concentrations of acid or buffer components were in large excess of the substrate concentration first order kinetics were observed.

The pathways between PSH and PS$^-$ are shown in Scheme 1; k_{H_2O}, k_{A^-}, and k_{OH^-} refer to the rate coefficients for proton abstraction from PSH by the solvent, general bases, and hydroxide ions respectively while k_{H^+}, k_{HA}, and k_{OH} are the rate coefficients for protonation of PS$^-$ by the hydronium ion, general acids, and the solvent. The results in Table 2 show the absence of buffer catalysis; for example changing the concentration of an acetic acid–sodium acetate buffer by a factor of 10 produced no measurable change in rate constant. This indicates that under our experimental conditions PSH and PS$^-$ are in rapid equilibrium and the internal cyclisation step is rate determining. Since, as shown previously, the equilibrium concentration of PS$^-$ will be small the observed rate constant can be expressed by equation (2). In solutions where p$h \leq 3$

$$k_{obs} = k_{-1} + k_1K[HO^-] \qquad (2)$$

the observed rate constant is independent of acidity giving a value for k_{-1} of 38 ± 2 s^{-1}. The data in less acidic solutions give the value of k_1K as $(4 \pm 1) \times 10^{10}$ l mol^{-1} s^{-1}. Combination of these results gives a value for KK_1 in good agreement with that determined independently from the measurement of equilibrium optical densities.

TABLE 2

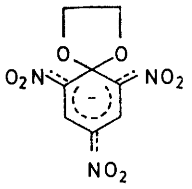
Kinetic data for the decomposition of (III)[a] in acidic buffers and in hydrochloric acid in water at 25°

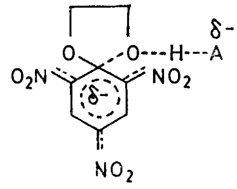
Acid	[HA]/ M	[Na$^+$A$^-$]/ M	pH	k_{obs}/ s^{-1}	$10^{-10}k_1K$[b]/ l mol^{-1} s^{-1}
Acetic	0.026	0.026	4.71	60 ± 2	4.3
	0.065	0.065	4.70	60	4.4
	0.13	0.13	4.72	60	4.2
	0.26	0.26	4.78	60	3.7
	0.039	0.013	4.2	46	5.0
Formic	0.026	0.026	3.65	40	
	0.065	0.065	3.62	40	
	0.13	0.13	3.60	39	
	0.26	0.26	3.60	37	
	0.039	0.013	3.22	39	
	0.19	0.065	3.17	37	
Chloroacetic	0.025	0.025	2.92	38	
	0.063	0.063	2.90	37	
	0.125	0.125	2.92	34	
	0.020	0.005	2.5	40	
	0.10	0.025	2.5	37	
	0.06	0.06	2.93	38	
	0.06[c]	0.06[c]	2.58	38	
Hydrogen phthalate	0.026	0.024	5.05	86	4.3
	0.021	0.029	5.20	120	5.1
Hydrochloric	0.025			39 ± 1	
	0.025[c]			38	
	0.005			38	
	0.005[c]			37	
	0.0075			39	
	0.0075			37	
	0.010			39	
	0.050			40	
	0.10			41	
	0.25			42	
DCl in D_2O	0.005			33 ± 1	

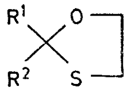
[a] Substrate concentration 1—3 × 10^{-5}M. Calculated value.
[c] Made up to ionic strength 0.25M with sodium chloride.

If as we expect the value of K is *ca.* 10^4 l mol^{-1} then k_1 will have a value of *ca.* 4×10^6 s^{-1}. This is a high value and we note that there may be experimental conditions, although we have not observed them, where proton transfer becomes rate determining[11] in Scheme 1. This will be the case when the cyclisation of PS$^-$ is a faster process than its protonation, *i.e.* $k_1 > k_{H^+}[H^+] + k_{HA}[HA] + k_{OH}$.

Catalysis of Ring-opening.—Previous studies with (V), the dioxolan analogue of (IV) have shown that ring-opening is subject to general acid catalysis.[12] The most probable mechanism involves concerted proton transfer and C–O bond cleavage with a transition state (VI). In contrast the data in Table 2 for complex (III) provide no evidence for catalysis by general acids. Indeed catalysis by hydronium ion is very feeble and not definitely established with experimental certainty. The data in Table 2 indicates also that ring-opening of (III) proceeds at rather similar rates in H_2O and D_2O with $k_{-1}(H_2O)/k_{-1}(D_2O)$ 1.15 ± 0.1, thus showing that the spontaneous reaction does not involve participation by the solvent.[13]


(V)


(VI)


(VII)

The finding that the dithiolan complex (III) is much less susceptible to acid catalysis than its dioxolan

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[11] *Cf.* C. Bernasconi and C. L. Gehriger, *J. Amer. Chem. Soc.*, 1974, **96**, 1092.

[12] M. R. Crampton and M. J. Willison, *J.C.S. Perkin II*, 1974, 1686.

[13] B. Capon, 'Organic Reaction Mechanism,' Wiley-Interscience, New York, 1972, p. 389.

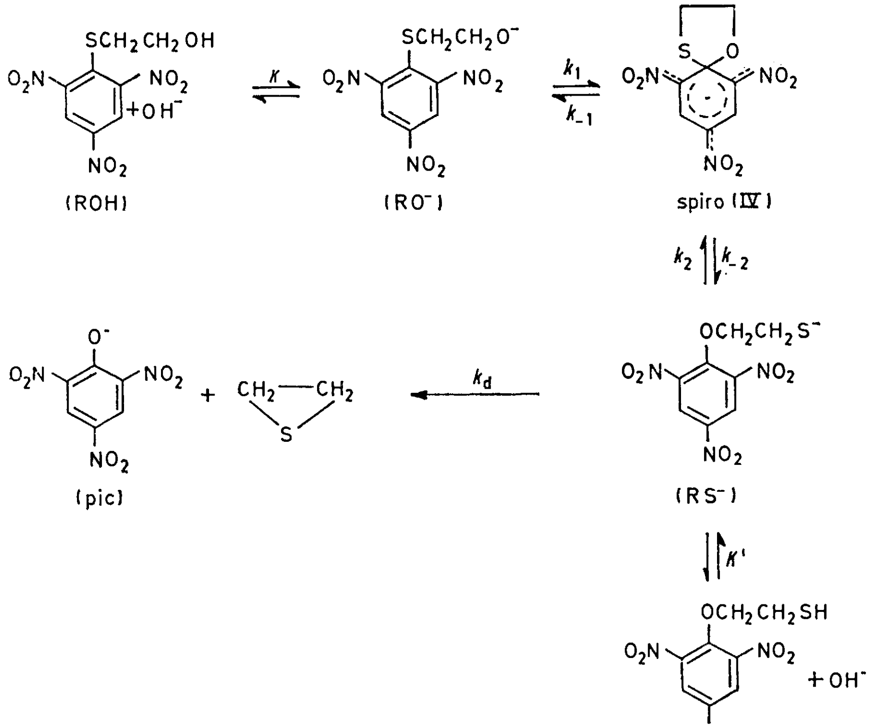
analogue (V) has relevance to previous studies[14-16] involving the neutral 1,3-oxathiolans (VII) (R^1,R^2 = H, alkyl, or Ph). It strongly suggests that the acid-catalysed decomposition of the latter compounds proceeds *via* oxygen-protonated species rather than by sulphur-protonated species.

TABLE 3

Mercury catalysed decomposition of complex (III) in water at 25°

$10^6[HgCl_2]$/M	10^5[Substrate]/M	Conditions	k_{obs}/s^{-1}
0	4	*a*	39
5	4	*a*	42
8	6	*a*	52
10	4	*a*	77
3	2	*b*	43
5	6	*b*	50
8	6	*b*	67
10	6	*b*	100

[a] Hydrochloric acid, 2.5×10^{-3}M. [b] Chloroacetate buffer, 0.025M, pH = 2.9.



SCHEME 2

The resistance to acid of the dithiolan complex (III) can be rationalised in terms of the low proton basicity of sulphur relative to oxygen.[17] It is however known[18,19] that sulphur, a 'soft' base, has a high affinity for mercury(II) ions, a 'soft' acid. The results in Table 3 show that the first-order rate coefficient for decomposition of (III) is dramatically increased by the presence of very low concentrations of mercury(II) chloride. The value of the catalytic coefficient appears to increase with increasing mercury concentration but has a value of at least 10^6 l mol^{-1} s^{-1}. A similar but less dramatic catalysis by mercuric ions has been noted[14] in the decomposition of (VII; R^1 = H, R^2 = Ph).

1-(2-*Hydroxyethylthio*)-2,4,6-*trinitrobenzene*.—It has previously been shown that in the presence of base 1-(2-hydroxyethylthio)-2,4-dinitrobenzene[9] and the analogous picryl compound[8,9] undergo reversed Smiles rearrangements with ultimate decomposition to ethylene sulphide and substituted phenol (2,4-dinitrophenol or picric acid respectively). Our equilibrium and kinetic data are discussed in terms of Scheme 2.

In the presence of dilute sodium hydroxide solution or aqueous alkaline buffers an aqueous solution of 1-(2-hydroxyethylthio)-2,4,6-trinitrobenzene gave a strong red colour, attributed to spiro-complex (IV), which slowly faded to yellow. The u.v.–visible spectrum of this final solution had $\lambda_{max.}$ 355 and 410 nm (shoulder) characteristic of the picrate ion.[20] The visible spectrum of the red intermediate, determined point by point using the stopped-flow spectrophotometer had $\lambda_{max.}$ 435 and 500 nm (shoulder) and was similar in shape to that of other picrylic Meisenheimer complexes.[2] The positions

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[14] N. C. De and L. R. Fedor, *J. Amer. Chem. Soc.*, 1968, **90**, 7266.

[15] T. H. Fife and L. K. Jao, *J. Amer. Chem. Soc.*, 1969, **91**, 4217.

[16] K. Pihlaja, *J. Amer. Chem. Soc.*, 1972, **94**, 3330.

[17] E. M. Arnett, *Progr. Phys. Org. Chem.*, 1963, **1**, 223.

[18] W. Stricks, I. M. Kolthoff, and A. Heyndrickx, *J. Amer. Chem. Soc.*, 1954, **76**, 1515.

[19] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

[20] M. R. Crampton, and M. A. El Ghariani, *J. Chem. Soc.* (*B*), 1969, 330.

of the absorption maxima are between those of the dioxolan complex (V), $\lambda_{\text{max.}}$ 417 and 470 nm,[3] and the dithiolan complex (III), $\lambda_{\text{max.}}$ 458 and 550 nm, and are thus consistent with structure (IV). ^{1}H N.m.r. spectra in aqueous DMSO (Experimental section) confirm the intermediacy of (IV) in that solvent. By use of the stopped-flow spectrophotometer it was possible to determine optical densities at 435 nm after completion of the initial colour-forming reaction but before appreciable fading to picrate. Values at various pH are given in Table 4 with calculated values of K_c. Kinetic measurements were made either in solutions where the base concentration was in large excess of the substrate concentration or in buffer solutions whose pH did not vary during the course of any one kinetic run. Under these conditions accurately first-order kinetics were observed. Values of the rate coefficients k_{obs}' for formation of the coloured intermediate and k_{obs}'' for its decomposition to picrate and ethylene sulphide are in Table 5. These values were independent of the wavelength of measurement.

TABLE 4

Equilibrium data for formation of (IV) from 1-(2-hydroxyethylthio)-2,4,6-trinitrobenzene in aqueous buffer at 25°

pH [a]	10^5[Substrate]/M	O.D.$_{435}$ [c]	$10^{-3}K_c$ [d]/l mol^{-1}
8.4	4.02	0.021	9.9
8.9	4.02	0.055	9.8
9.15	6.1	0.133	8.0
9.45	4.02	0.142	7.0
9.50	4.27	0.168	7.0
9.75	4.27	0.240	6.3
9.88	4.02	0.325	7.9
12 [b]	4.02	0.87	

[a] Borax buffers, 0.0125M. [b] Sodium hydroxide, 10^{-2}M. [c] For 1 cm pathlength cell. [d] K_c is defined as O.D.$_{435}$/(0.87 − O.D.$_{435}$)[OH$^-$].

TABLE 5

Kinetic data for reaction of 1-(2-hydroxyethylthio)-2,4,6-trinitrobenzene with base in water at 25°

pH [a]	[OH$^-$]/M	k'_{obs}/s^{-1}	k''_{obs}/s^{-1}
9.15	1.4×10^{-5}	2.46 ± 0.05	0.025
9.50	3.2×10^{-5}	2.65	0.043
9.75	5.6×10^{-5}	2.95	0.061
9.88	7.6×10^{-5}	3.55	0.089
10.2	1.6×10^{-4}	4.3	0.117
10.4	2.5×10^{-4}	5.6	0.134
10.6	4×10^{-4}	6.6	0.151
	0.01 [b]		0.22
	0.05 [b]		0.21
	0.10 [b]		0.20

[a] Borax buffers, 0.0125M. [b] Sodium hydroxide.

In order to interpret these data we will assume that the proton transfer steps in Scheme 2 are fast. By analogy with previous work [3] the value of K (= [RO$^-$]/[ROH][OH$^-$]) is likely to be *ca.* 10^{-1} l mol^{-1} so that at the base concentrations used the proportion of substrate present as RO$^-$ will be small. The work of Smiles [21] indicates that the proportion of thiol ether (RSH) present in equilibrium with the parent (ROH) will be small. (The observation of a reversed Smiles rearrangement here derives from the irreversible decomposition of RS$^-$. The well known ability of sulphur to form three-membered rings [22] and the excellent leaving group ability of the picrate ion will contribute to the ease of this decomposition). However the value of K' (= [RS$^-$]/[RSH][HO$^-$]) is expected to be similar to that, *ca.* 10^4 l mol^{-1}, for complex (III). Hence the possibility remains that a considerable proportion of the substrate is present as RS$^-$. However the optical density measurements in Table 4 shows that the apparent extinction coefficient of (IV) is 2.2×10^4 l mol^{-1} cm^{-1} which is in the range 2—3×10^4 l mol^{-1} cm^{-1} expected for such complexes.[2] Thus it is possible to achieve nearly complete conversion of the substrate to spiro-complex (IV), indicating a value for K_2 (= [spiro]/[RS$^-$]) of >5. We conclude therefore that the substrate is present very largely in the forms ROH, spiro, and pic. In this circumstance the value for K_c of 8×10^3 l mol^{-1} corresponds to KK_1, and the rate coefficient for the fast colour forming reaction is related to k_1 and k_{-1} by equation (3).

$$k_{\text{obs}}' = Kk_1[\text{OH}^-] + k_{-1} \tag{3}$$

A plot of k_{obs}' *versus* [OH$^-$] is linear with intercept (k_{-1}) 2.2 ± 0.2 s^{-1} and slope (Kk_1) $(1.3 \pm 0.3) \times 10^4$ l mol^{-1} s^{-1}. Combination of these kinetic data gives a value for KK_1 of 6×10^3 l mol^{-1} in reasonable agreement with the value obtained from optical density measurements.

The rate-limiting step in the decomposition of (IV) to picrate and ethylene sulphide might be cleavage of the C–S bond in the spiro-complex (k_{-2}) or elimination of ethylene sulphide from RS$^-$ (k_d). If C–S bond breaking is rate-limiting the data in Table 5 lead to a value for k_{-2} of 0.2 s^{-1}. This value is an order of magnitude lower than that calculated for k_{-1}, the rate constant for C–O bond breaking in (IV). Since C–S bond breaking in an intermediate such as (IV) might be expected to be faster than C–O bond-breaking [23] it seems unlikely that this is rate limiting. The alternative possibility that k_d is rate determining leads to equation (4).

$$\frac{1}{k_{\text{obs}}''} = \frac{K_2}{k_d} + \frac{K_2}{k_d} \cdot \frac{1}{KK_1[\text{OH}^-]} \tag{4}$$

A plot of $1/k_{\text{obs}}''$ *versus* 1/[OH$^-$] gives a straight line with intercept (K_2/k_d) 5 ± 0.5 s and slope ($K_2/k_d \,.\, KK_1$) $6 \pm 0.5 \times 10^{-4}$ s mol l^{-1}. Combination of slope and intercept gives a value for KK_1 of $(8 \pm 0.5) \times 10^3$ l mol^{-1} in good agreement with that determined independently.

Comparison of Complexes (III)—(V).—Equilibrium and kinetic data are summarised in Table 6. For consistency the values of (III) and (V) have been statistically corrected (experimental k_{-1} divided by two, and experimental KK_1 and K_1 multiplied by two).

The high value of KK_1 for complex (III) indicates the

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[21] N. J. Evans and S. Smiles, *J. Chem. Soc.*, 1935, 181.

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high thermodynamic stability of this complex. 1-(2-Mercaptoethylthio)-2,4,6-trinitrobenzene will cyclise in water buffered at pH 5. However since thiols have considerably lower pK_a values than corresponding alcohols,[10] leading to higher values for K, the value of K_1, the equilibrium constant governing interval cyclisation of the anion, will be about three orders of magnitude smaller for (III) than for (V). This result is perhaps surprising in view of the high carbon basicities previously found[5] for sulphur bases relative to oxygen bases. For example the equilibrium constants for addition of methoxide and thioethoxide ions to 1,3,5-trinitrobenzene to give σ-complexes have values of 23 and 3 500 l mol^{-1} respectively. However in the case of 1,3,5-trinitrobenzene base addition occurs at an unsubstituted ring position. Cyclisation of the thiolate ion intermediate in the formation of (III) involves addition at a carbon carrying a thioether group while corresponding alkoxide addition in the formation of (V) involves addition at a carbon carrying an ether group. It has been suggested[24] that a major factor contributing to the high stability of 1,1-dialkoxy-complexes is the special stabilising effect of two or more electronegative substituents attached to an sp^3 hybridised carbon atom.[25] The stabilisation should be much less important with two sulphur atoms at C-1 than with two oxygen atoms. In this context it is relevant to note Biggi's and Pietra observation[6] that addition of ethanethiolate to ethyl thiopicrate gives a mixture of 1,1- and 1,3-adducts with the latter predominating. A second factor contributing to the relative instability of 1,1-bisalkylthio-complexes may be destabilisation resulting from steric interactions between two sulphur atoms at the same carbon atom.

TABLE 6

Equilibrium and kinetic data for spiro-complex formation [a] in water at 25°

	Complex (III)	(V)	(IV)
$KK_1{}^b$/l mol^{-1}	2×10^9	3.6×10^7	8×10^3
$K_1{}^b$	2×10^5	3.6×10^8	8×10^4
k_1K/l mol^{-1} s^{-1}	4×10^{10}	1.6×10^6	1.3×10^4
k_1/s^{-1}	4×10^6	1.6×10^7	1.3×10^5
$k_{-1}{}^b$/s^{-1}	19	0.05	2.2

[a] Assuming values for K of 10^{-1} for (IV) and (V), and 10^4 for (III). [b] Statistically corrected.

The kinetic data show that the difference in values of K_1 for (III) and (V) derives mainly from the difference in k_{-1} values, reflecting the greater ease of C–S than C–O bond breaking. The values of k_1, allowing for uncertainties resulting from the estimation of K values, are not very different.

The data for (IV) refer to formation of the complex from 1-(2-hydroxyethylthio)-2,4,6-trinitrobenzene so that comparison with (V) is relevant. Our results do not allow the calculation of similar parameters for complex formation from 1-(2-mercaptoethoxy)-2,4,6-trinitrobenzene. The reduced stability of (IV) compared with (V), reflecting a lower value of k_1 and higher value of k_{-1}, can be accounted for in a number of ways. Again the stabilising effect of multiple alkoxy-substitution will favour (V) relative to (IV) and replacement of oxygen by sulphur would be expected to introduce steric effects. Also polarisation of the ether linkage $(\overset{\delta+}{\mathrm{C}}\text{–}\overset{\delta-}{\mathrm{O}})$ in the parent which will encourage nucleophilic attack at C-1 will be considerably reduced in thioether due to the lower electronegativity of sulphur. It is relevant to note here that methoxide addition to 1-methylthio-2,4,6-trinitrobenzene is reported[26] to give the 1,3- rather than a 1,1-adduct.

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