Kinetics of the Desulphuration of ^{35}S-Labelled Thiourea in Sodium Hydroxide studied by Chromatographic Methods

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The kinetics of the desulphuration of ^{35}S-labelled thiourea in aqueous solutions of carbon dioxide-free sodium hydroxide has been studied at 80—100 °C in the range pH 12—13. The undecomposed thiourea and the sulphide ion were separated by paper chromatography and their radioactivity was measured. The desulphuration may be considered to be a second-order reaction $S{=}C(NH_2)_2 + OH^- \longrightarrow NCNH_2 + SH^- + H_2O$. The rate constants are sensitive to the ionic strength of the medium. An activation energy of 18 ± 1 kcal mol^{-1} was obtained.

THE isomerization of thiourea (Tu) to ammonium thiocyanate in acid and salt aqueous solutions (90—130 °C) [1] and in molten mixtures of thiourea and ammonium thiocyanate [2,3] is first order with respect to thiourea. In alkaline solutions thiourea first gives sodium sulphide and cyanamide (CA) which is then transformed into dicyanamide, amidinourea, guanidine or, at pH > 12, almost quantitatively into urea (U); this isomerizes to ammonium cyanate which is then hydrolysed to ammonium carbonate. Kosareva *et al.*[4] studied the kinetics of the thiourea desulphuration in NaOH at different concentrations in the range 80—120 °C and concluded that it is first order with respect to sodium hydroxide and to thiourea. The results of this investigation are questionable because (*a*) the experiments were done in sealed glass tubes which are attacked by the alkali,[5] (*b*) it is doubtful that the analytical methods used give very accurate quantitative data, and (*c*) the rate constants were evaluated by using the tangent of the initial part of the curve obtained by plotting log ($[\mathrm{Tu}_0]/[\mathrm{Tu}_t]$) *versus* t. We have therefore re-examined the kinetics of this reaction by (*a*) using Teflon containers and ^{35}S-labelled thiourea, (*b*) separating the thiourea from the sulphide ions by paper chromatography, and (*c*) determining their quantities by radioactivity measurements.

EXPERIMENTAL

A 0·2M aqueous solution of ^{35}S-labelled thiourea, diluted with inactive thiourea, was prepared with water twice distilled under nitrogen in order to exclude carbon dioxide. A 0·2M aqueous solution of NaOH was prepared by diluting under nitrogen a Normex solution (C. Erba) of pure NaOH with the same carbon dioxide-free water. The solutions were kept under nitrogen in an automated apparatus from which measured volumes of the solutions were directly transferred into the reaction containers under nitrogen.

Only in one series of experiments were Pyrex glass tubes of *ca.* 0·2 ml capacity used for comparison. After filling them with the solution they were sealed and hermetically closed in a steel container with some drops of water in order to counterbalance the internal pressure of the glass tube on warming. The other experiments were done using Teflon containers of the same capacity hermetically sealed in a steel container.

pH Measurements were performed at 100 °C, the solution first being quenched at room temperature, in Teflon containers of *ca.* 2 ml capacity under nitrogen. The measurements were made in a thermostat (±0·1 °C) using a microelectrode Metrohom EA 125U (pH = 0—14) particularly suited for measurements at high pH connected with a Polymetron 42B apparatus reading 0·01 pH units.

An aqueous solution of zinc acetate (0·02 ml) were dried on one side of a strip of chromatographic paper (35 × 1 cm). The reacted solution (0·02 ml) was then superimposed on the spot of zinc acetate in order to fix the sulphide ions as ZnS. Thiourea was then eluted in a compact spot on the strip by the ascending method with n-butanol–ethanol–0·1M aqueous ammonium acetate (4 : 1 : 2). Zinc acetate does not interfere with the elution of thiourea. Preliminary experiments showed that up to 100 °C, in the solutions used and for the times explored, no thiocyanate is formed and therefore all the transformed thiourea gives only sulphide ions.

The ratioactivity of the sulphide and thiourea spots was determined with a Geiger–Muller counter with a 10 × 10 mm slit by measuring successive contiguous areas of the strip. The sum of the radioactivities of thiourea and sulphide spots was always equal to that of the starting thiourea.

RESULTS AND DISCUSSION

The experimental values of the concentrations $[\mathrm{S}^{*2-}]$ determined after time t at temperature T in the solutions having starting concentrations [Tu*] and [NaOH] are given in Table 1. By assuming that in the desulphuration reaction (1) the OH$^-$ consumption equals the SH$^-$ formation and by putting $[S{=}C(NH_2)_2] = [\mathrm{Tu}^*] = a$, $[OH^-] = b$, and $[SH^-]=[S^{*2-}] = x$ in the second-order rate law $\mathrm{d}x/\mathrm{d}t = k(a - x)(b - x)$ the rate constants k were calculated.

$$S{=}C(NH_2)_2 + OH^- \longrightarrow NC{\cdot}NH_2 + SH^- + H_2O \qquad (1)$$

Plots of $1/(a - x)$ (Figure 1) or $\log (a - x)/(b - x)$ *versus* t are linear for all NaOH solutions in Teflon; In Figure 2 the values of $\log [b(a - x)]/[a(b - x)]$ *versus* t are reported in order to have a common origin for the different curves. In all the experiments (Tu : NaOH ratios from 5 to 0·2 and NaOH concentrations varying from 0·1 to 0·02M) the k values are satisfactorily constant over the whole range of times explored. The plot of $\log k$ *versus* $1/T$ is linear (Figure 3) and gives the values

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TABLE 1

Kinetics of the desulphuration of ^{35}S-labelled thiourea (Tu*) in aqueous solutions of NaOH; 10^5k in l mol^{-1} s^{-1}

Container	Teflon		Teflon		Teflon		Teflon		Teflon		Teflon		Teflon		Glass	
T/°C	100		100		80		90		100		100		100		100	
10^5[Tu*]/M	10,000		10,000		10,000		10,000		10,000		5000		2000		10,000	
10^5[NaOH]/M	2000	(a)	5000	(b)	10,000	(c)	10,000	(d)	10,000	(e)	10,000	(f)	10,000	(g)	10,000	(h)
t/h	[S^{*2-}]	k	[S^{*2-}]	k	[S*]$^{2-}$	k	[S*]$^{2-}$	k	[S^{*2-}]	k	[S^{*2-}]	k	[S^{*2-}]	k	[S^{*2-}]	k
1									349	10·1	224	12·9			312	8·95
									363	10·5						
2	163	11·9	395	11·7	199	2·82	375	5·41	663	9·8	407	12·0	201	14·8	628	9·31
	214	15·9	384	11·3	184	2·60	384	5·55	726	10·9	372	10·9	196	14·5		
3									1093	11·4	622	12·7			779	7·82
									1085	11·3						
4	284	10·8	703	10·9	390	2·82	747	5·61	1266	10·1	765	12·0	376	14·7	1030	7·97
	278	10·6	691	10·7	414	3·00	735	5·51	1355	10·9	752	11·8	374	14·6		
6	393	10·3	958	10·4	554	2·71	1076	5·58	1846	10·5	1084	12·0	510	14·1	1435	7·76
	442	11·9	1020	11·2	506	2·47	1038	5·36	1876	10·7			498	13·6		
7	450	10·4														
	466	10·8														
8	493	10·1	1272	10·9	677	2·52	1311	5·24	2246	10·1	1310	11·3	592	12·6	1576	6·50
	464	9·6	1210	10·3	673	2·51	1292	5·15	2272	10·2			624	13·4		
10	615	10·6	1416	10·0	852	2·59	1743	5·86	2560	9·6	1497	10·8	762	13·9	1712	5·74
	611	10·5	1427	10·1	818	2·48	1730	5·81	2749	10·5	1520	11·0	742	13·4		
12	812	12·6			987	2·54	1959	5·64	2982	9·8	1667	10·3	893	14·4	1914	5·48
	760	11·5			1004	2·58	1934	5·55	2948	9·7	1722	10·8	902	14·6		
15	882	11·3			1252	2·65	2299	5·53	3458	9·8	1918	10·0	1024	14·1	2047	4·77
	884	11·4			1217	2·57	2283	5·48	3549	10·2			1046	14·6		
20															2328	4·21
Mean value		10·9		10·7		2·63		5·51		10·3		11·4		14·1		

TABLE 2

k Values calculated from the data of [Tu] at time t given in ref. 4 for solutions of [Tu] = 0·0360 and [NaOH] = 0·1M at 120 °C, in glass containers

t/h	[Tu]/mM	[CA]/mM	[U]/mM	10^5k_1/s^{-1}	10^4k_2/ l mol^{-1} s^{-1}
0·08	35·0	1·4		9·2	14·1
0·25	33·7	2·4	3·5	7·3	7·4
0·5	31·4	3·3	2·8	7·6	7·8
1	29·8	2·3	4·3	5·3	5·4
1·5	28·2	2·0	4·3	4·5	4·7
2	26·4	1·7	5·3	4·3	4·5
4	21·2	2·7	3·3	3·7	4·0
6	18·6	3·4	3·1	3·1	3·4
12	13·7	4·7	2·3	2·2	2·6
24	10·2	3·9	3·4	1·5	1·7
48	6·2	4·1	2·9	1·0	1·3
72	4·7	5·6	1·4	0·79	1·0
96	3·9	4·8	1·9	0·64	0·83
120	2·9	5·0	3·5	0·58	0·77

in Table 3 for the energy of activation. The mean value is close to that of 16 ± 2 kcal mol^{-1} obtained by Kosareva *et al.*[4]

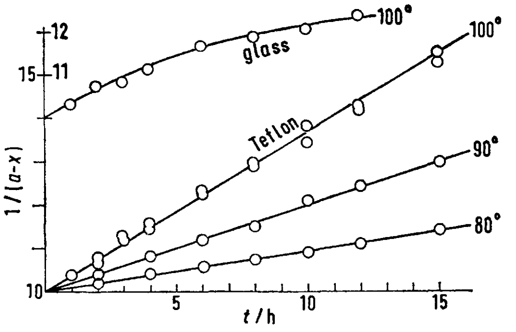

FIGURE 1 Plots of $1/(a-x)$ *versus* t for solutions of thiourea (0·1M) and NaOH (0·1M) at 80, 90, and 100 °C, in Teflon containers. The values obtained in Pyrex containers at 100 °C are also reported

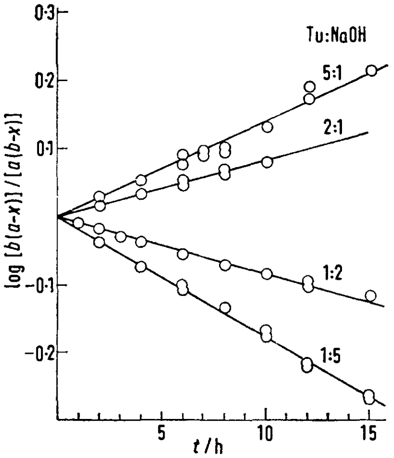

FIGURE 2 Plots of log $[b(a-x)]/[a(b-x)]$ *versus* t for solutions of thiourea and NaOH in the ratios 0·1 : 0·02, 0·1 : 0·05, and 0·05 : 0·1, at 100 °C. a = [Tu], b = [OH$^-$]

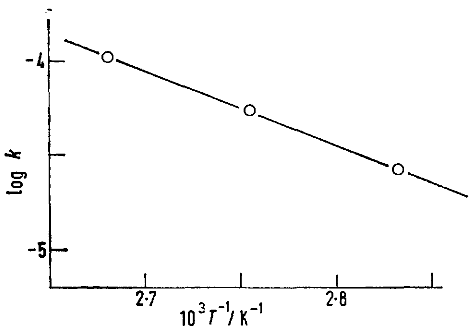

FIGURE 3 Arrhenius plot for the desulphuration of thiourea at 80, 90, and 100 °C

By calculating the ionic strength $\mu = \frac{1}{2}C_iZ_i^2$ [6] from the NaOH concentration and plotting k *versus* $\mu^{\frac{1}{2}}$ (Figure 4) a straight line is obtained; the extrapolation

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[6] S. W. Benson, 'Chemical Kinetics,' McGraw-Hill, New York, 1960, p. 525.

to $\mu = 0$ gives $k_0 = 11 . 1\cdot10^{-5}$. The plot of log (k/k_0) *versus* $\mu^{\frac{1}{2}}$ (Figure 4) is linear.

TABLE 3

$T_2 - T_1$/°C	E/kcal mol^{-1}
100—90	16·8
90—80	18·9
100—80	17·9
Mean value	18 ± 1

The rate constants calculated for both a first- and a second-order reaction (assuming $[OH^-]$ consumed equal to $[SH^-]$ formed) from the data obtained by Kosareva *et al.*[4] (Table 2) in glass containers decrease very rapidly with time.

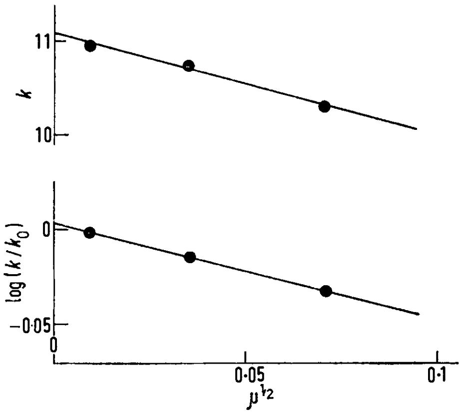


FIGURE 4 Plots of k and of log (k/k_0) *versus* $\mu^{\frac{1}{2}}$ (μ = ionic strength) for solutions of Tu (0·1M) and NaOH at concentration of 0·02, 0·05, and 0·1M

The rate constant of desulphuration measured in glass containers [Table 1(h)] decreases with time presumably on account of the consumption of NaOH by the glass.

The pH measurements at room temperature (Table 4) indicate that a certain amount of OH^- is consumed by the reaction. If the OH^- concentration is calculated from the pH values, taking into account the OH^- activities at the different concentrations,[7] then the OH^- consumption is greater than that corresponding to the desulphuration reaction (1) assumed for the calculation of the rate constants.

It was shown by Buchanam and Barsky[8] that cyanamide, at pH 12·6—13·6 and 50 °C, is almost quantitatively hydrolysed to urea, and by Warner[9] that urea, above pH 12 and at 100 °C, is isomerized to ammonium cyanate and that potassium cyanate, in 0·1M-NaOH at 100 °C, is hydrolysed to ammonium carbonate. The three reactions follow a first-order rate law. From these rate constants one might expect that cyanamide and urea should be practically absent from the system. Kosareva *et al.*[4] found in their solutions (Table 2) 5—15% of cyanamide and *ca.* 10% of urea, calculated on the starting thiourea, from 0·25 to 120 h. This discrepancy is perhaps due to the fact that all these experiments[4,9,10] were performed in glass vessels. Anyhow these data show that cyanate and carbonate ion are formed very early in the reaction and may be responsible for the OH^- consumption observed (Table 4) being greater than that corresponding to reaction (1). The calculations of rate constants were based on reaction (1) assuming that the OH^- consumption equals the SH^- formation. Such a simplification does not seem to affect the results, however, as is shown by the rather good and consistent values obtained for different Tu : NaOH ratios and at different temperatures.

TABLE 4

pH Values measured at T_0 for aqueous solutions warmed at 100 °C

Container	Teflon	Teflon	Teflon	Glass	Glass
T/°C	23	25	22	25	22·5
[Tu]/M	0·10	0·05	0·02	0·10	0
[NaOH]/M	0·10	0·10	0·10	0·10	0·10
t/h	(e)	(f)	(g)	(h)	
0	12·96	12·89	13·00	12·89	12·97
1	12·95	12·86		12·86	12·96
2	12·94	12·84	13·00	12·81	12·95
3	12·91	12·80		12·76	12·91
4	12·89	12·76	13·00	12·72	12·89
6	12·85	12·73	12·99	12·66	12·85
8	12·77	12·70	12·99	12·54	12·84
10	12·75	12·64	12·98	12·42	12·83
12	12·73	12·60	12·97	12·28	12·81
15	12·63	12·53	12·96	11·91	12·80
20	12·39		12·94	11·04	12·79

$$NC(NH_2)_2 + H_2O \longrightarrow O{=}C(NH_2)_2 \tag{2}$$

$$O{=}C(NH_2)_2 \longrightarrow NH_4CNO \tag{3}$$

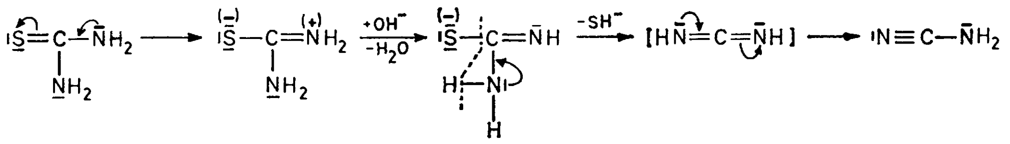
$$OCN^- + 2H_2O \longrightarrow HCO_3^- + NH_3 \tag{4}$$

$$k_2 = 8\cdot10^{-2}\,s^{-1} \text{ at } 50°C \tag{5}$$

$$k_3 = 0\cdot15\,s^{-1} \text{ at } 100°C \tag{6}$$

$$k_4 = 0\cdot18\,s^{-1} \text{ at } 100°C \tag{7}$$

It is known that thiourea behaves as a zwitterion[10,11] which may play a role in the thiourea desulphuration. A tentative mechanism of this reaction is suggested in the Scheme.



SCHEME

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