

The Reaction Between Carbon Disulphide and Azide Ions

A Kinetic Investigation

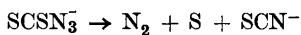
NIELS HOFMAN-BANG and BIRTHE HOLTEN

Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark

Sommer¹ was the first to observe that carbon disulphide and azide ions interact with the formation of azido-dithiocarbonate ions, SCSN_3^- . A kinetic study of this reaction was of interest because Hofman-Bang and Szybalski² found that the rate determining reaction step of the carbon disulphide catalyzed iodine-azide reaction was a second order reaction between carbon disulphide molecules and azide ions. Further it was shown³ that this iodine-azide reaction was a chain reaction with a chain length of about 17 at room temperature, and that the chain length was almost independent of temperature. From these results it could be inferred that the energy of activation of the reaction between azide ions and carbon disulphide could not differ greatly from that of the iodine-azide reaction, and that the ratio between the rate constants of the two reactions would be identical with the chain length of the iodine-azide reaction. The experiments confirmed these expectations.

ANALYTICAL METHOD

Introductory experiments showed that the formation of azido-dithiocarbonate ions was accompanied by the formation of a very small percentage of partly colloidal sulphur, and therefore spectrophotometric measurements were left out of consideration. The formation of these small amounts of sulphur was presumably due to slow decomposition of azido-dithiocarbonate ions. Currier and Browne⁴ found that a solution of sodium azido-dithiocarbonate was slowly decomposed according to the scheme:



Browne and Smith ⁵ investigated possible methods for the determination of azido-dithiocarbonate ions when no interfering substances were present. The best method was found to be a Volhard titration. The procedure was as follows:

The sample of azido-dithiocarbonate was dissolved in about 125 ml of water, a few drops of conc. nitric acid were added, and thereafter 0.05 *N* silver nitrate solution was added to an excess of about 10 ml. The mixture was allowed to settle for two hours. The precipitated silver azido-dithiocarbonate was removed by filtration and the filtrate and wash water were treated with 2 ml of a 10 % solution of ferric alum which contained one fourth of its volume of nitric acid. The excess of silver was then determined by titration with a standard solution of ammonium thiocyanate to the appearance of a permanent red coloration. The error of this determination was 0.1–0.2 %.

This Volhard titration was modified so that the amount of azido-dithiocarbonate could be estimated when an excess of sodium azide and carbon disulphide was present. In water the solubility of silver azido-dithiocarbonate, AgSCSN_3 , was found ⁵ to be 2.2×10^{-4} mole per liter at 25° C. According to Browne *et al.*⁶ azido-dithiocarbonic acid, in contradistinction to hydrazoic acid, is a fairly strong acid. So, although the solubility in water of silver azide ⁷ is only 5.1×10^{-5} mole per liter at 25° C, it was to be expected that

Table 1. Effect of concentration of nitric acid on the Volhard titration of azido-dithiocarbonate ions. 10 ml solution containing 1.025 millimole sodium azido-dithiocarbonate was diluted with 125 ml water or 1, 2 or 4 *M* nitric acid. Silver nitrate (0.05074 *M*) was added to an excess of 5–10 ml. After two hours the mixture was filtered, and the filtrate and wash water, after addition of ferric alum, were titrated with standard ammonium thiocyanate solution (0.05460 *M*).

Expt. no.	Conc. of nitric acid	Silver nitrate added, ml	Ammonium thiocyanate added, ml	Azido-dithiocarbonate found	
				millimole	%
1	0	27.29	6.60	1.023	100
2	0	27.67	6.88	1.027	
3	1 <i>M</i>	28.04	7.47	1.014	98.6
4	1 »	28.29	7.82	1.007	
5	2 »	28.43	7.82	1.014	99.0
6	2 »	28.37	7.75	1.015	
7	4 »	28.40	7.86	1.009	98.6
8	4 »	28.45	7.86	1.013	

Table 2. Effect of sodium azide and carbon disulphide on the Volhard titration of azido-dithiocarbonate ions in 4 M nitric acid. 10 ml solution containing varying amounts of sodium azido-dithiocarbonate was diluted with 125 ml 4 M nitric acid in which approx. 0.1 g carbon disulphide and 0.2 g sodium azide had been dissolved. Silver nitrate solution (0.05074 M) was added to an excess of 5–10 ml. After two hours the mixture was filtered and the precipitate washed with 50 ml 4 M nitric acid. The filtrate and wash solution, after addition of ferric alum, were titrated with standard ammonium thiocyanate solution (0.05460 M).

Expt. no.	Azido-dithio-carbonate added, millimole	Silver nitrate added, ml	Ammonium thiocyanate added, ml	Azido-dithio-carbonate found	
				millimole	%
1	1.025	27.13	6.46	1.023	99.7
2	1.025	27.65	6.99	1.020	
3	0.5125	17.20	6.69	0.5074	99.3
4	0.5125	18.14	7.51	0.5104	
5	0.2563	14.70	9.05	0.2518	98.4
6	0.2563	15.52	9.80	0.2524	
7	0.1025	10.06	7.47	0.1025	101.0
8	0.1025	10.80	8.12	0.1046	

silver azido-dithiocarbonate could be precipitated in strong nitric acid without co-precipitation of silver azide.

Firstly, experiments were carried out to determine if silver azido-dithiocarbonate was precipitated quantitatively when rather much nitric acid was present. Expt. nos. 1 and 2 in Table 1 represent the analysis of a standard solution of sodium azido-dithiocarbonate. 10.00 ml of this solution was diluted with 125 ml water and the estimation was carried out exactly according to the procedure of Browne and Smith⁵. In expt. nos. 3 and 4, 125 ml 1 M nitric acid was added instead of 125 ml water, but the remaining procedure was unchanged. Even when using 4 M nitric acid the error was less than 2 %.

In the experiments in Table 2 different, but known amounts of sodium azido-dithiocarbonate were estimated by Volhard titration in 4 M nitric acid and in the presence of ca. 0.1 g carbon disulphide and 0.2 g sodium azide. In acid solution carbon disulphide would not be expected to react with silver ions, and no further formation of azido-dithiocarbonate ions would be expected to take place, because azide ions only, and not hydrazoic acid, will react with carbon disulphide. If considerably more than 0.2 g sodium azide was present,

a redbrown colour, due to a complex formed between ferric ions and azide ions, would appear when ferric alum was added. According to Ricca⁸ the dominating complex ion seems to be FeN_3^{++} , so it is quite understandable that the redbrown colour did not appear in 4 *M* nitric acid when the added amount of sodium azide was not too large, because the ionization constant of hydrazoic acid is about 2×10^{-5} at 25° C. The redbrown ferric azide colour would have prevented the titration with thiocyanate.

The results (see Table 2) showed that the estimation could be carried out within an error of 1—2 %.

EXPERIMENTAL

The analytical method developed above was used for the determination of the degree of conversion in an aqueous solution of carbon disulphide and an excess of sodium azide. A kinetic experiment was carried out as follows:

Two 500 ml measuring flasks containing sodium azide and carbon disulphide solution respectively, were placed in the thermostat water for the sake of temperature adjustment. The sodium azide solution was made by weighing dried sodium azide and dissolving in the measuring flask. The sodium azide used was analyzed by oxidizing hydrazoic acid to free nitrogen by means of ceric salt⁹ in excess. The purity was found to be 99.8 %. The carbon disulphide solution of about the concentration required, was made by dilution of a saturated aqueous solution.

The sodium azide solution was now poured into a 1000 ml bottle with an outlet at the bottom. The outlet was provided with a piece of rubber tubing and a Mohr tubing compressor. The experiment was started by pouring the carbon disulphide solution down into the sodium azide solution. When half the carbon disulphide solution had run out of the measuring flask, a stopwatch was started. Thereafter the bottle was stoppered and shaken for ten seconds, and the mixture was distributed as quickly as possible — through the rubber tubing — among ten 60 ml bottles which were stoppered immediately so that no air at all was present between mixture and stopper, and then placed in the thermostat. The first and the last bottles thus filled were left at room temperature until next day, and then used for the determination of the initial concentration of carbon disulphide.

After a certain time of reaction (*t*) one of the bottles in the thermostat was opened and 10 to 50 ml of the mixture was taken out with a pipette and run into a suitable amount of nitric acid so that the total volume was 135 ml and the molar concentration of nitric acid 4, whereby further formation of azido-dithiocarbonate ions was prevented. Then the determination of azido-dithiocarbonate was carried out exactly as described above. The most convenient method for the determination of the initial concentration of carbon disulphide was to allow the two samples mentioned above to react until complete conversion of carbon disulphide into azido-dithiocarbonate ions — with a following determination of these. In all cases 24 hours at 20° C were enough to secure complete conversion (more than 99.9 %).

As was to be expected, the reaction turned out to be a second order reaction with respect to azide ions and carbon disulphide molecules. In

Table 3. The bimolecular reaction between azide ions and carbon disulphide molecules at 20° C. *a* and *b* are the initial molar concentrations of sodium azide and carbon disulphide respectively; *t* is the time of reaction in minutes; *x* is the molar concentration of azido-dithiocarbonate ions at the time *t*; *k* is the second order rate constant calculated according to (1).

Expt. no.	1		2		3	
<i>a</i>	0.03079		0.03077		0.06154	
<i>b</i>	0.004127		0.007923		0.01290	
<i>t</i>	10 ³ · <i>x</i>	<i>k</i>	10 ³ · <i>x</i>	<i>k</i>	10 ³ · <i>x</i>	<i>k</i>
15 min			0.83	0.243	2.48	0.236
30 »			1.63	0.256	4.60	0.249
60 »	1.47	0.244	2.81	0.250	7.27	0.241
90 »					8.96	0.235
120 »	2.34	0.237	4.43	0.242	10.64	0.266
150 »					11.24	0.253
180 »	2.91	0.234	5.50	0.240	11.77	0.254
240 »	3.33	0.240	6.22	0.239		
300 »	3.56	0.232	6.69	0.235		
360 »			6.96	0.225		
Average		0.237		0.241		0.248

Table 3 are given the details of three experiments with different initial concentrations. The corresponding rate constant *k* (for each time of reaction *t*) was calculated from the integrated second order rate expression:

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

where *a* is the initial concentration of sodium azide, *b* is the initial concentration of carbon disulphide, and *x* is the concentration of azido-dithiocarbonate ions at the time *t*.

ENERGY OF ACTIVATION

The energy of activation of the formation of azido-dithiocarbonate ions was determined by experiments analogous to those described above. The rate of reaction was determined by experiments analogous to those described above. The rate of reaction was determined in the temperature range 8° to 25° C. In

Table 4. Energy of activation of the reaction between azide ions and carbon disulphide. a and b are the initial molar concentrations of sodium azide and carbon disulphide respectively; t is the time of reaction in minutes; x is the molar concentration of azido-dithiocarbonate ions at the time t ; k is the second order rate constant calculated according to (1). $k_{exp.}$ is the simple average of the k values in one experiment. $k_{calc.}$ was calculated from the equation $\log k = H - \frac{A}{T}$, which is a straight line fitted to the experimental $k_{exp.}$ and T (abs. temperature) values.

Expt. no.	1		2		3		4		5	
	a	0.06154	0.06153	0.06154	0.06154	0.06154	0.06154	0.06154	0.06154	
b		0.01042	0.01378	0.01548	0.01290	0.01246				
Temp. °C		7.68	10.00	15.00	20.00	25.00				
t	$10^3 \cdot x$	k	$10^3 \cdot x$	k	$10^3 \cdot x$	k	$10^3 \cdot x$	k	$10^3 \cdot x$	k
15 min.							2.48	0.236	4.04	0.440
30 »							4.60	0.249	6.70	0.446
45 »									8.65	0.468
60 »			2.99	0.0679	5.74	0.1322	7.27	0.241	9.71	0.455
75 »									10.43	0.443
90 »					7.78	0.1359	8.96	0.235		
120 »	3.28	0.0527	5.38	0.0704	9.20	0.1340	10.64	0.266		
150 »							11.24	0.253		
180 »	4.37	0.0511	6.97	0.0680	11.40	0.1362	11.77	0.254		
210 »										
240 »	5.30	0.0506	8.45	0.0700	12.59	0.1311				
360 »	6.49	0.0469	10.22	0.0682						
480 »	7.70	0.0493	11.44	0.0684						
$k_{exp.}$		0.0501		0.0683		0.134		0.248		0.450
$k_{calc.}$		0.0502		0.0684		0.131		0.246		0.452

Table 4 is given the average rate constant ($k_{exp.}$) for each temperature. Using the method of least squares, the numerical values of H and A were calculated according to the equation:

$$\log k = H - \frac{A}{T}$$

where k is the rate constant and T is the absolute temperature, giving:

$$\log k = 15.147 - \frac{4618}{T}$$

By inserting the experimental values for T , values of k ($k_{calc.}$) were calculated. These are also given in Table 4. The energy of activation was:

$$A \times 4.571 = 4618 \times 4.571 = 21100 \text{ cal/mole}$$

The frequency exponent H , which had the value 15.15 using minutes as the time unit, was $15.15 - \log 60 = 13.37$ with seconds as the unit.

At 20° C the rate constant of the carbon disulphide catalyzed iodine-azide reaction ² was found to be 4.45, while that of the formation of azido-dithiocarbonate ions (see Table 3) was 0.248. The ratio between the two constants is 18.0; the chain length of the iodine-azide reaction was found ³ to be about 17 at room temperature.

The energy of activation of the iodine-azide reaction was found ² to be 19950 cal, *i. e.* only 1150 cal less than that of the reaction between azide ions and carbon disulphide. These 1150 cal represent the negative energy of activation of the chain length of the iodine-azide reaction.

SUMMARY

The reaction between azide ions and carbon disulphide with formation of azido-dithiocarbonate ions was investigated kinetically. It is a second order reaction with respect to azide ions and carbon disulphide molecules. The energy of activation was found to be 21100 cal/mole. The values of the rate constant confirmed that this reaction is closely related to the carbon disulphide catalyzed iodine-azide reaction.

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