

The Iodine-Azide Reaction

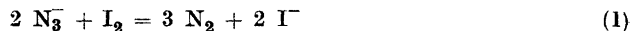
II. The Catalytic Effect of Carbon Disulphide

NIELS HOFMAN-BANG and WACLAW SZYBALSKI

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

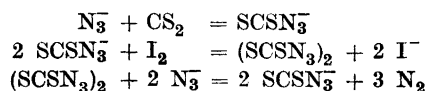
In connection with the senior author's investigations on the iodine-azide reaction, it was of obvious interest to examine the kinetics with carbon disulphide as catalyst.

The overall equation of the iodine-azide reaction is:



This reaction takes place only if a suitable catalyst is present. Substances which contain sulphide sulphur, in general, act as catalysts.

Browne and Hoel¹ were the first to ascertain that carbon disulphide also will catalyze the iodine-azide reaction. These authors have investigated the stoichiometry of this process and found excellent conformity with equation (1). Furthermore, it has been shown that if carbon disulphide vapour is bubbled through an aqueous solution of sodium or potassium azide, exactly one mole carbon disulphide per mole azide will be gradually absorbed with the formation of one mole of alkali azido-dithiocarbonate. If iodine solution is added to such a solution of azido-dithiocarbonate, a white precipitate of azido-carbon disulphide will be formed. The last mentioned compound together with sodium azide solution gives a brisk evolution of nitrogen, while at the same time reduction to azido-dithiocarbonate ions possibly takes place. On the basis of the above mentioned experiences, the following mechanism for the iodine-azide reaction with carbon disulphide as the catalyst was proposed:



after which the azido-dithiocarbonate ions again react with iodine, and so on. Browne and Hoel emphasize that the azido-dithiocarbonate ions are the actual catalyst, and that the formation of this ion is irreversible, so that no carbon disulphide is regenerated after it has once become "fixed".

Feigl and Chargaff² — apparently without having noticed the work of Browne and Hoel — have also dealt with the catalytic action of carbon disulphide on the iodine azide reaction. Partly on the basis of various qualitative experiments and partly on Sommer's³ observation that carbon disulphide and azide ions react with the formation of azido-dithiocarbonate ions, a reaction mechanism was proposed nearly identical to that of Browne and Hoel. The only difference was that Feigl and Chargaff assumed that carbon disulphide is regenerated when the reaction takes place. The investigations recorded in the present paper agree with the mechanism of Feigl and Chargaff, and the formation of azido-dithiocarbonate ions has been found to be the rate determining reaction step.

EXPERIMENTAL

N. Hofman-Bang⁴ has shown that the rate of the iodine-azide reaction — catalyzed by tetrathionate ions — is proportional to the concentration of azide ions and tetrathionate ions, but independent of the concentration of iodine. Therefore it was possible to make kinetic experiments by adding a small amount of iodine solution together with some starch solution, to a solution of sodium azide and potassium tetrathionate. When the quantity of iodine was used up, the solution changed momentarily from a blue colour to colourless, and thus it was easy to measure the reaction time. It soon became evident that the rate of the carbon disulphide catalyzed iodine-azide reaction was also independent of the iodine concentration, for which reason an analogous experimental method could be applied.

Experimental procedure (for further details see ref. 4): Into a 500 ml Erlenmeyer flask was pipetted iodine in potassium iodide, sodium azide, sodium perchlorate, starch indicator, and water; and the flask was placed in a water thermostat, so that only the neck was above the water. After the elapse of 30 minutes (for sake of temperature adjustment) an aqueous solution (usually 10 ml) of carbon disulphide was sucked into a pipette. The solution was immediately allowed to run down in the Erlenmeyer flask, which at the same time — partly immersed in the thermostat water — was kept in a rotary motion with the left hand. When half of the carbon disulphide solution had run out of the pipette, a stopwatch was started. The last drop in the pipette was blown out, and the flask was kept rotating for an additional 10 sec. The instant the blue colour of the solution disappeared, a new portion of iodine was added from a pipette, and the time of reaction was determined again. The volume of iodine solution added was small — usually 0.1—0.5 ml — in relation to the total volume of the reacting solution (250 ml). In nearly all the experiments carried out five portions of iodine solution were added one after another. The addition of the first portion of iodine solution — especially if operating

with a small quantity of iodine — does not always yield such fine results as the following portions, because the experimental solution usually consumes a small amount of iodine itself.

As soon as this work was started, it became evident that it was necessary to find an easy method for the direct determination of the concentration of carbon disulphide in an aqueous solution. For that reason the well known iodometric determination of carbon disulphide was modified⁵ so that titration with iodine could be used even if carbon disulphide was on hand in a dilute aqueous solution. The determinations of carbon disulphide were carried out, in all the present series of experiments, in the following way: immediately after taking out 10 ml carbon disulphide solution for the catalytic experiment, another 10 ml was removed and was allowed to run down into 20 ml 10 % alcoholic potash contained in a 300 ml Erlenmeyer flask with glass stopper. After replacing the stopper, the flask was shaken for a few seconds and left in darkness for 30 minutes. Thereafter the stopper was removed and washed with a small amount of water, one drop of phenolphthalein was added, and neutralization by dropwise addition of 60 % acetic acid took place. An excess of 3—4 drops was added. For the sake of imparting to the solution an adequate reaction one gram of calcium carbonate was added, and the flask shaken for about 15 seconds. After the addition of 1 ml of starch indicator, the solution was diluted with oxygen-free water to 150 ml and titrated with 0.01 *N* iodine. The iodine solution was added to an excess of about 0.5 ml. The excess was determined by back titration with 0.01 *N* thiosulphate.

Solutions used: The iodine solution was 0.100 *N* to iodine and 0.180 *M* to potassium iodide. In the experiments the iodine solution was added by means of a Krogh syringe pipette. The sodium azide solution was made 0.1000 *M* by weighing out pure sodium azide (analyzed according to⁴) and dissolving in a volumetric flask. The solutions of potassium iodide and of sodium perchlorate were also made 0.1000 *M* by weighing out the calculated amounts of the pure, dried salts.

EFFECT OF IODINE CONCENTRATION

From Table 1 it can be seen that the rate of reaction is, as a whole, independent of the iodine concentration. But the rate seems to be somewhat slower if the iodine concentration is very low (Expt. no. 6). This phenomenon is perhaps related to the fact that iodine is bound to starch and therefore does not react quite so readily as does free iodine. In all experiments 10 ml of 0.1 *M* potassium iodide were added in order to keep the iodide concentration constant during an experiment, as the reduction of iodine to iodide otherwise would cause a considerable percentile change. Furthermore, the colour change of the starch indicator will be more abrupt and sharp if the concentration of iodide ions is fairly large. The ionic strength was kept constant (0.02) in all experiments by the addition of varying amounts of 0.1 *M* sodium perchlorate. The concentrations of potassium and perchlorate ions were in no case so high that precipitation of potassium perchlorate took place. From t_3 (the time of

reaction for the third addition of iodine) was calculated the corresponding rate constant k_3 , according to the second order rate expression:

$$k = \frac{2.303}{c \cdot t} \cdot \log \frac{a}{a-x} \quad (2)$$

where c is the concentration of carbon disulphide, t is the time of reaction, a is the initial concentration of sodium azide, and $a - x$ is the concentration of sodium azide to the time t . Analogously was calculated, from the experimental times of reaction, the rate constants k_2 , k_4 and k_5 . From these constants together with k_3 , the average k_a was taken, which is given in the table.

Table 1. Effect of iodine concentration on the reaction between sodium azide and iodine at 20° C.

Catalyst: Carbon disulphide. In all experiments — besides the solutions mentioned in the table — were added 1 ml 0.5 % starch indicator, 10 ml 0.1 M potassium iodide, and water, so that the total volume was 250 ml. The added amounts of iodine in potassium iodide, sodium azide, carbon disulphide and sodium perchlorate are given in ml 0.1 N solution. t_3 is the reaction time for the third addition of iodine, k_3 is the corresponding rate constant. k_a is the average of k_2 , k_3 , k_4 and k_5 . Ionic strength in all experiments: 0.02.

Expt. no.	Iodine solution		Sodium azide	Carbon disulphide	Sodium perchlorate	t_3 min	k_3	k_a
	Iodine	Potassium iodide						
1	0.40	0.72	25	0.78	14.2	12.28	4.35	4.35
2	0.40	0.72	25	0.78	14.2	12.28	4.35	4.32
3	0.80	1.44	25	0.98	13.5	20.27	4.38	4.38
4	1.60	2.88	25	0.90	12.1	47.86	4.42	4.40
5	0.50	0.90	12.5	0.47	26.6	52.73	4.49	4.47
6	0.10	0.18	12.5	0.50	27.3	10.48	3.90	3.87

EFFECT OF CARBON DISULPHIDE CONCENTRATION

From Table 2 it can be seen that the rate of reaction is proportional to the concentration of carbon disulphide. From Expt. no. 1 to Expt. no. 8 the

Table 2. *Effect of carbon disulphide concentration on the reaction between sodium azide and iodine at 20° C.*

Catalyst: Carbon disulphide. In experiments 1, 2, 3 and 4 — besides the solutions mentioned in the table — were added 1 ml 0.5 % starch indicator, 10 ml 0.1 *M* potassium iodide, and water, so that the total volume was 250 ml. In experiments 5, 6, 7 and 8 were added the same solutions except that the 10 ml 0.1 *M* potassium iodide was replaced by 10 ml 0.1 *M* sodium perchlorate. The added amounts of iodine in potassium iodide, sodium azide, carbon disulphide, and sodium perchlorate are given in ml 0.1 *N* solution. t_3 is the reaction time for the third addition of iodine, k_3 is the corresponding rate constant. k_a is the average of k_2 , k_3 , k_4 and k_5 . Ionic strength in all experiments: 0.02.

Expt. no.	Iodine solution		Sodium azide	Carbon disulphide	Sodium perchlorate	t_3 min	k_3	k_a
	Iodine	Potassium iodide						
1	0.40	0.72	25	1.44	14.2	6.42	4.51	4.46
2	»	»	»	0.73	»	12.57	4.54	4.52
3	»	»	»	0.37	»	25.11	4.49	4.47
4	»	»	»	0.19	»	48.75	4.50	4.46
5	0.10	0.18	1.25	1.46	38.6	39.00	4.40	4.38
6	»	»	»	2.79	»	21.47	4.18	4.19
7	»	»	»	5.64	»	10.48	4.23	4.23
8	»	»	»	10.80	»	5.60	4.14	4.05

relation between the concentrations of azide and carbon disulphide is changed by a factor of about 10^3 , but nevertheless, the difference between the two corresponding rate constants is only approx. 10 %.

EFFECT OF SODIUM AZIDE CONCENTRATION

Table 3 shows that the rate of reaction is proportional to the concentration of sodium azide.

Table 3. Effect of sodium azide concentration on the reaction between sodium azide and iodine at 20° C.

Catalyst: Carbon disulphide. In all experiments — besides the solutions mentioned in the table — were added 1 ml 0.5 % starch indicator, 10 ml 0.1 *M* potassium iodide and water, so that the total volume was 250 ml. The added amounts of iodine in potassium iodide, sodium azide, carbon disulphide, and sodium perchlorate, are given in ml 0.1 *N* solution. t_3 is the reaction time for the third addition of iodine, k_3 is the corresponding rate constant. k_a is the average of k_2, k_3, k_4 and k_5 . Ionic strength in all experiments: 0.02.

Expt. no.	Iodine solution		Sodium azide	Carbon disulphide	Sodium perchlorate	t_3 min	k_3	k_a
	Iodine	Potassium iodide						
1	0.50	0.90	6.25	0.477	32.70	123.07	4.26	4.25
2	»	»	12.50	0.488	26.60	53.28	4.28	4.25
3	»	»	12.50	0.497	26.60	52.32	4.27	4.25
4	»	»	25.00	0.504	14.10	24.60	4.24	4.20

EFFECT OF IONIC STRENGTH

Since the rate of the carbon disulphide catalyzed iodine-azide reaction is directly proportional to the concentration of sodium azide and to the concentration of carbon disulphide, it is reasonable to assume that the rate determining reaction step is a reaction between azide ions and carbon disulphide molecules



An investigation of the primary salt effect might support this assumption. According to Brønsted⁶ the ratio between the rate constant at ionic strength 0.1 and the rate constant at ionic strength 0.02 should be about one, when an ion of one charge reacts with a neutral molecule. From Table 4 it is seen that the experimental ratio is 1.005, which agrees well with the assumption made as to the rate determining step.

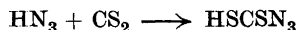
Table 4. Effect of ionic strength on the reaction between sodium azide and iodine at 20° C.

Catalyst: Carbon disulphide. In the two experiments — besides the solutions mentioned in the table — were added 1 ml 0.5 % starch indicator, 10 ml 0.1 *M* potassium iodide, and water, so that the total volume was 250 ml. The added amounts of iodine in potassium iodide, sodium azide, carbon disulphide, and sodium perchlorate are given in ml 0.1 *N* solution. t_3 is the reaction time for the third addition of iodine, k_3 is the corresponding rate constant. k_a is the average of k_2 , k_3 , k_4 and k_5 . Ionic strength in Expt. 1 is 0.02, and in Expt. 2 it is 0.1.

Expt. no.	Iodine solution		Sodium azide	Carbon disulphide	Sodium perchlorate	t_3 min	k_3	k_a
	Iodine	Potassium iodide						
1	0.50	0.90	12.5	1.58	26.60	15.73	4.47	4.41
2	»	»	»	1.36	226.60	18.22	4.48	4.43

EFFECT OF pH

According to Brønsted⁶ a reaction between two un-charged molecules would show a very small primary salt effect, for which reason the reaction



would also agree with the salt effect found. Hydrazoic acid is an acid of about the same strength as acetic acid, *i. e.* the acid constant is approx. 10^{-5} . In a sodium azide solution, with $\text{pH} > 7$, the concentration of un-ionized hydrazoic acid will be proportional to the concentration of hydrogen ions, or, if the pH decreases by 1, the concentration of hydrazoic acid increases ten times. As can be seen from Table 5, a variation of pH does not change the rate constant. For this reason the rate determining step cannot be a reaction between hydrazoic acid and carbon disulphide.

A few experiments have been carried out with identical concentrations of sodium azide, carbon disulphide, and iodine. In addition, varying amounts of perchloric acid were added, so that the azide ions were partly converted into un-ionized hydrazoic acid. The rate of reaction gradually decreases as the conversion of the azide ions into hydrazoic acid proceeds, and when a small excess of perchloric acid (or another strong acid) is added, the rate of reaction becomes extremely small. Consequently we have good reasons to assume that only free azide ions — and not hydrazoic acid — take part in the reaction.

Table 5. Effect of pH on the rate of the reaction between sodium azide and iodine at 20° C.

Catalyst: Carbon disulphide. In the experiments — besides the solutions mentioned in the table — were added 1 ml 0.5 % starch indicator, 10 ml 0.1 *M* potassium iodide, 0.1 *M* boric acid, and 0.1 *N* sodium hydroxide, so that the total volume was 250 ml. The added amounts of iodine in potassium iodide, sodium azide, and carbon disulphide are given in ml 0.1 *N* solution. t_3 is the reaction time for the third addition of iodine, k_3 is the corresponding rate constant, k_a is the average of k_2, k_3, k_4 and k_5 . The given values of pH were measured by means of a glass electrode.

Expt. no.	Iodine solution		Sodium azide	Carbon disulphide	pH	t_3 min	k_3	k_a
	Iodine	Potassium iodide						
1	0.50	0.90	12.5	1.55	7.80	15.93	4.50	4.44
2	»	»	»	1.54	7.80	15.98	4.52	4.52
3	»	»	»	1.53	8.40	16.10	4.50	4.50
4	»	»	»	1.53	8.80	16.00	4.55	4.46

ENERGY OF ACTIVATION

The energy of activation of the carbon disulphide catalyzed iodine-azide reaction was determined by experiments analogous with those previously described. The rate of reaction was determined in the temperature range 0.4 to 20° C. Due to the volatility of carbon disulphide from an aqueous solution, it was impossible to use temperatures higher than 20° C. But at 20° C or less, the loss of carbon disulphide during an experiment was negligible (this is also the reason why all the previous experiments were carried out at 20° C — and not 25° C). In Table 6 are given the average values of the rate constant, k_a . Using the method of least squares, the numerical values of H and A were calculated according to the equation:

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

where T is the absolute temperature. The result is

$$\log k_a = 15.537 - \frac{4364}{T}$$

From this equation values of k were calculated by substituting T with the experimental temperatures. These values are, together with the experimental ones, recorded in Table 6. The energy of activation is:

$$A \times 4.571 = 19\,950 \text{ kcal/mole}$$

The frequency exponent H , which has a value of 15.537 with 1 min as time unit, is — with 1 sec. as unit — $15.537 - \log 60 = 13.759$.

Table 6. Energy of activation of the carbon disulphide catalyzed iodine-azide reaction.

In all experiments — besides the carbon disulphide solution — were added 1 ml starch indicator, 10 ml 0.1 M potassium iodide, 12.5 ml 0.1 M sodium azide, 0.50 ml 0.1 N iodine, which was 0.18 M with respect to potassium iodide, 26.60 ml 0.1 M sodium perchlorate, and water, so that the total volume was 250 ml. The added amounts of carbon disulphide are given in ml 0.1 M solution. t_3 is the reaction time for the third addition of iodine, k_3 is the corresponding rate constant; k_a is the average of k_2, k_3, k_4 and k_5 . $k_{calc.}$ was calculated from the equation $\log k_a = H - \frac{A}{T}$, which is a straight line fitted to the experimental k_a and T values. Ionic strength in the experiments: 0.02.

Expt. no.	Temp. °C	Carbon disulphide	t_3 min	k_3	k_a	$k_{calc.}$
1	20	0.470	52.38	4.52	4.44	4.45
2	»	0.500	49.40	4.50	4.49	
3	15	0.925	51.03	2.35	2.33	2.45
4	»	0.940	48.37	2.44	2.39	
5	12.5	1.675	36.87	1.80	1.82	1.81
6	»	1.695	36.73	1.79	1.80	
7	10	1.530	52.65	1.38	1.40	1.33
8	»	1.546	52.67	1.37	1.38	
9	0.4	2.230	138.47	0.360	0.375	0.380
10	»	2.165	139.72	0.367	0.375	

IS CARBON DISULPHIDE OR AZIDO-DITHIOCARBONATE IONS THE ACTUAL CATALYST?

In order to ascertain whether or not the carbon disulphide that combines with azide ions in accordance with equation (3), is subsequently regenerated during the following stages of the iodine-azide reaction, Browne and Hoel¹

have carried out an experiment as follows: 'A sample of pure, dry, solid potassium azido-dithiocarbonate, weighing 0.1974 g, was dissolved in 20 cc of a 20 % solution of potassium trinitride. A concentrated solution of iodine, in potassium iodide, was introduced, drop by drop, below the surface of the solution, while a slow current of air was continuously bubbled through the reacting mixture and then through an alcoholic solution of potassium hydroxide. The azido-salt used would correspond to a total weight of carbon disulphide amounting to 0.0955 g. No indication whatever of the presence of carbon disulphide in the gases from the flask was obtained when the alcoholic solution was tested in the usual way with acetic acid and copper sulfate, although the operation of bubbling air through the flask was continued for 20 minutes.'

From this experiment Browne and Hoel concluded that azido-dithiocarbonate is the actual catalyst, and that no carbon disulphide is regenerated after it has become 'fixed' as azido-dithiocarbonate. This assumption does not agree with our kinetic experiments. If this assumption were true, the rate of reaction in an experiment would increase until all carbon disulphide present had combined with azide ions. We always found the rate of reaction strictly proportional to the concentration of carbon disulphide, and the interaction between azide ions and carbon disulphide is known to be a slow process.

We have carried out two experiments as follows: Into a Friedrichs gas washing bottle were introduced 50 ml 0.1 *M* sodium azide, an amount of carbon disulphide solution corresponding to 2.00×10^{-4} mole carbon disulphide, 1 ml starch indicator, and water, to a total volume of 90 ml. This solution was allowed to stand for one hour, so that the carbon disulphide would be partly 'fixed' as azido-dithiocarbonate ions. After addition of a further 10 ml of water, a constant air current was bubbled through the solution for 10 minutes. The carbon disulphide vapour contained in the air current was absorbed in another Friedrichs bottle containing 30 ml 10 % alcoholic potash, and estimated — by iodine titration — to be 1.03×10^{-4} moles. Consequently, 0.97×10^{-4} moles of carbon disulphide had been converted into azido-dithiocarbonate ions. A parallel experiment was carried out differing only in that after 1 hour 10 ml 0.1 *N* iodine solution was added instead of 10 ml of water. The amount of carbon disulphide driven off by the air current was estimated to be 1.82×10^{-4} moles. From a control experiment it was found that only a negligible amount of iodine was volatilized during the aeration. These experiments show that carbon disulphide was regenerated when the iodine-azide reaction took place. The probable reason why Browne and Hoel found no regeneration is that they added iodine drop by drop so that only small amounts of carbon disulphide were liberated; and, due to the

extremely high concentration of sodium azide (20 %), the re-formation of azido-dithiocarbonate ions took place before the carbon disulphide had a chance to escape.

IODINE AZIDE, IN_3

As can be seen below, it is a possibility that iodine azide, IN_3 , is an intermediate product in the iodine-azide reaction. If so, iodine azide would have to react vigorously with azide ions with the formation of free nitrogen. An aqueous solution of iodine azide was prepared according to Hantzsch⁷. All operations were carried out at + 5° C. The solution was mixed with a 5 % solution of sodium azide (at + 5° C). Only very slow liberation of a gas took place — possibly due to spontaneous decay of iodine azide.

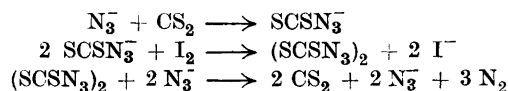
DISCUSSION

From all the experiments mentioned it is evident that the rate of the carbon disulphide catalyzed iodine-azide reaction is proportional to the concentration of carbon disulphide, proportional to the concentration of free azide ions, and independent of the concentration of iodine. Therefore, the rate determining reaction step must be:



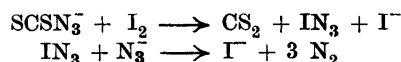
The reverse of this reaction is without importance in this case, and the formation of azido-dithiocarbonate ions has been shown^{1, 3} to take place even if iodine is not present. Therefore it is reasonable to assume that it is also the *first* step in a sequence of reactions. Investigations by Browne, Smith, Gross and Brandes⁸ on the conductivity of the azido-dithiocarbonate ion have shown that azido-dithiocarbonic acid is a moderately strong acid, and hence only azido-dithiocarbonate ions will be on hand in slightly basic solution.

As the reactions in which iodine takes part are instantaneous, it is impossible by simple kinetic investigations to elucidate them further. Since Browne and Hoel¹ have shown that iodine reacts immediately with azido-dithiocarbonate ions with formation of azido-carbon disulphide, which again reacts with sodium azide solution with the evolution of nitrogen, it is reasonable to assume a reaction mechanism rather similar to that of Browne and Hoel.



This mechanism differs from the one proposed by Browne and Hoel only in that carbon disulphide — and not only azido-dithiocarbonate ions — is regenerated.

Possible reaction steps — after the formation of azidodithiocarbonate ions — could also be:



but as iodine azide does not react — or at least only very slowly — with azide ions, this possibility must be excluded.

SUMMARY

Kinetic investigations have been carried out on the iodine-azide reaction catalyzed by carbon disulphide. The reaction is a second order reaction as to azide ions and carbon disulphide molecules. The rate of reaction was found to be independent of the concentration of iodine. The investigations agree with a reaction mechanism rather similar to that proposed by Browne and Hoel¹. The difference is that carbon disulphide — and not azido-dithiocarbonate ions — must be considered as the actual catalyst. The relation between rate constant and absolute temperature has been found to be

$$\log_{10} k = 13.759 - \frac{4364}{T}$$

with seconds as the time unit, and k calculated in natural logarithms. The energy of activation is 19 950 kcal/mole.

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