

The Iodine-Azide Reaction

IV. Chain Length of the Carbon Disulphide Catalyzed Reaction

NIELS HOFMAN-BANG

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

The kinetics of the iodine-azide reaction, which is a reaction between azide ions and iodine, has been studied by Dodd and Griffith¹, Hofman-Bang^{2, 3}, and Hofman-Bang and Szybalski⁴, with potassium tetra- and pentathionate and carbon disulphide as the catalysts. The general picture is that the rate of reaction is proportional to the concentration of azide ions and catalyst, but independent of the concentration of iodine. The rate determining reaction step must therefore be a reaction between an azide ion and a catalyst ion or molecule. In the case of the carbon disulphide catalyzed iodine-azide reaction⁴, the rate determining reaction step is without doubt the *first* reaction step in a sequence of reactions. The present author has mentioned² that the tetrathionate catalyzed iodine-azide reaction seems to be analogous, so that the *first* and rate determining reaction step is a reaction between an azide ion and a tetrathionate ion.

That a reaction takes place between azide ions and tetrathionate ions even if iodine is not present, can be shown by a rather simple experiment: Stock solutions of 0.1 *M* sodium azide, 0.05 *M* potassium tetrathionate, and 0.02 *N* iodine in 0.04 *M* potassium iodide, were kept at 25° C in a water thermostat. 10 ml potassium tetrathionate solution, 10 ml sodium azide, and 0.2 ml starch indicator were mixed in an Erlenmeyer flask and left for *t* minutes in the thermostat. 10 ml iodine solution was now added, and after an additional *t'* minutes the iodine-starch colour disappeared. From Table 1 it can be seen that when the time *t* was longer than approx. 20 minutes the reaction with iodine was instantaneous.

Quite analogous experiments could be carried out with carbon disulphide instead of potassium tetrathionate. In this case the product formed by interaction between azide ions and carbon disulphide molecules is known to be

Table 1. Reaction between sodium azide and potassium tetrathionate at 25° C. 10 ml 0.05 M potassium tetrathionate were mixed with 10 ml 0.1 M sodium azide solution and 0.2 ml starch indicator, and left for t minutes. 10 ml 0.02 N iodine solution was now added, and after an additional t' minutes the iodine-starch colour disappeared.

Expt. no.	t Time in min	t' Time in min
1	0	12.18
2	5	10.02
3	10	7.18
4	15	3.87
5	20	0.78
6	25	0.00
7	30	0.00

azido-dithiocarbonate ions⁴⁻⁶. Such experiments with carbon disulphide showed that the ratio: number of iodine atoms consumed instantaneously per carbon disulphide molecule present, gradually increased with time to about 16. This shows that a chain reaction must take place.

CHAIN LENGTH OF THE CARBON DISULPHIDE CATALYZED IODINE-AZIDE REACTION

If a very diluted solution of sodium azide, a known amount of iodine, and starch indicator is titrated by dropwise addition of a diluted solution of sodium azido-dithiocarbonate until the iodine-starch colour disappears, it is to be expected that the ratio: atoms of iodine consumed per molecule of azido-dithiocarbonate should be about 16. It is, of course, a condition that the solutions are so diluted that any recombination of carbon disulphide molecules and azide ions to azido-dithiocarbonate ions can be neglected.

EXPERIMENTAL

Solutions used in the experiments: 1) A sodium azide solution, which was 0.1000 M; 2) an iodine solution, which was 0.00991 N with respect to iodine and 0.02 M to potassium iodide; 3) a sodium azido-dithiocarbonate solution, which was 0.0996 M. Sodium

Table 2. Determination of the chain length of the carbon disulphide catalyzed iodine-azide reaction. In each experiment were mixed 10 ml 0.1 M sodium azide, 10 or 20 ml 0.00991 N iodine, 1 ml starch indicator, and a considerable volume of water. This solution was titrated by dropwise addition of a 0.00198 M sodium azido-dithiocarbonate solution until the iodine-starch colour disappeared.

Expt. no.	Total volume ml	Sodium azide ml	Iodine ml	Sodium azido-dithiocarbonate used ml	Temp. of the solution °C	Chain length (atoms of iodine consumed per molecule of sodium azido-dithiocarbonate added)
1	500	10	10	3.18	23.2	15.7
2	250	10	10	2.93	23.1	17.1
3	500	10	10	3.10	14.1	16.1
4	500	10	20	5.99	23.7	16.7
5	500	10	10	3.10	34.2	16.1
6	500	10	10	3.06	24.1	16.4
7	1000	10	10	3.18	24.1	15.7

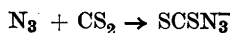
azido-dithiocarbonate was prepared according to Sommer⁵ and analyzed according to Browne and Smith⁷, who have worked out a modified Volhard titration for the determination of azido-dithiocarbonate. Before use 10 ml of the stock solution of sodium azido-dithiocarbonate were diluted with water to 500 ml. In each experiment 10 ml 0.1 M sodium azide, 10 or 20 ml 0.00991 N iodine, and 1 ml 0.5 % starch indicator were pipetted off into a 2 liter Erlenmeyer flask. After dilution with a considerable volume of water this solution was titrated with 0.00198 M sodium azido-dithiocarbonate solution. The flask was shaken vigorously after the addition of each drop of the azido-dithiocarbonate solution.

From Table 2 it is seen that the number of atoms of iodine consumed per molecule of sodium azido-dithiocarbonate added is fairly constant in all 7 experiments. It is independent of the azide ion concentration, the iodine concentration, and the temperature. Of course, there might be a slight dependency on temperature — which is not seen due to the experimental error. When the solution of sodium azide and iodine was titrated with a solution of sodium azido-dithiocarbonate 5 times stronger than the one used in the experiments, the results were about the same.

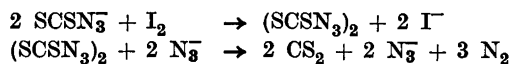
These results show that the carbon disulphide catalyzed iodine-azide reaction is a chain reaction with a chain length of 16—17 at room temperature.

DISCUSSION

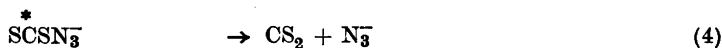
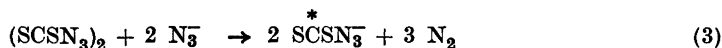
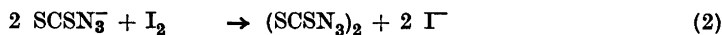
Kinetic investigations⁴ have shown that the rate determining reaction step of the carbon disulphide catalyzed iodine-azide reaction is formation of azido-dithiocarbonate ions:



Since Browne and Hoel⁶ 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 that the following reaction steps take place:



Due to the above mentioned results, which show that the reaction is a chain reaction with a chain length of 16—17, the reaction mechanism must be assumed to be somewhat different. The chain reaction can be accounted for by the following sequence of reactions:



In this sequence, reaction (1) is the rate determining, and all the other reactions are assumed to be very fast. The ion $\overset{*}{\text{SCSN}_3^-}$ in reaction (3) is assumed to be an activated ion, which can either decompose to a carbon disulphide molecule and an azide ion (reaction (4)) or give off energy to become an ordinary azido-dithiocarbonate ion (reaction (4a)). Two of these ions now can again react with iodine to give azido-carbon disulphide. Further it is necessary to assume that the activated ion $\overset{*}{\text{SCSN}_3^-}$ has a given probability of decomposing to carbon disulphide and azide, and consequently also a given probability of becoming an ordinary azido-dithiocarbonate ion. The probability must be independent of all concentrations and can according to the experiments only be very slightly dependent on the temperature. Let us

assume that the probability of decomposing into a carbon disulphide molecule and an azide ion is $\frac{1}{17}$. The chain length, S, would then be:

$$S = 1 + (1 - \frac{1}{17}) + (1 - \frac{1}{17})^2 + (1 - \frac{1}{17})^3 + \dots = 17$$

From the proposed chain mechanism can be inferred that the energy of activation of the reaction between azide ions and carbon disulphide must be about the same as that of the carbon disulphide catalyzed iodine-azide reaction, because the chain length is rather independent of temperature. This has already proved to be true (*cf.* a following publication).

To decide if tetra- and pentathionate ions combine with azide ions to form ions analogous to azido-dithiocarbonate ions, is difficult because a chemical reaction takes place with the evolution of nitrogen^{2,3}. When a solution of potassium tetra- or pentathionate and sodium azide was left for some time and then allowed to run down into a solution of iodine and sodium azide, several molecules of iodine per molecule of polythionate were consumed immediately. Therefore it seems reasonable also in these two cases to assume a chain reaction taking place with intermediates analogous to azido-dithiocarbonate ions. A kinetic study of the nitrogen evolution from a solution containing tetra-thionate and azide ions, could possibly give some valuable information.

SUMMARY

The catalytic effect of azido-dithiocarbonate ions on diluted solutions of iodine and sodium azide was studied. The reaction turned out to be a chain reaction with a chain length of about 17 at room temperature. A reaction mechanism has been proposed, in which the chain carrier is azido-dithiocarbonate ions. The chain length is independent of or only slightly dependent on the temperature. It was shown that tetra- and pentathionate ions react with azide ions with formation of a product which will give an instantaneous iodine-azide reaction.

REFERENCES

1. Dodd, G., and Griffith, R. O. *Trans. Faraday Soc.* **45** (1949) 546.
2. Hofman-Bang, N. *Acta Chem. Scand.* **3** (1949) 872.
3. Hofman-Bang, N. *Ibid.* **4** (1950) 456.
4. Hofman-Bang, N., and Szybalski, W. *Ibid.* **3** (1949) 1418.
5. Sommer, F. *Ber.* **48** (1915) 1833.
6. Browne, A. W., and Hoel, A. B. *J. Am. Chem. Soc.* **44** (1922) 2106.
7. Browne, A. W., and Smith, G. B. L. *Ibid.* **47** (1925) 2691.

Received April 20, 1950.