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XXXVII.—The Action of Bromine on Sodium and Silver Azides.

By DOUGLAS ARTHUR SPENCER.

Part I. Bromoazoimide.

DURING the course of experiments, suggested by Professor H. B. Baker, aiming at the preparation of triatomic nitrogen, bromine vapour, diluted with nitrogen, was passed over sodium azide. The colour of the gaseous mixture faded considerably, but was not completely discharged however long the bromine remained in contact with the azide, and the gas leaving the apparatus had a pungent but sickly smell reminiscent of hydrazoic acid and dilute bromine vapour.

An aqueous solution of the gas was yellow, gave a blood-red coloration with ferric chloride, smelled of hypobromous and hydrazoic acids, and slowly evolved nitrogen on standing.

Preliminary attempts to freeze out any compound formed resulted in violent explosions which occasionally detonated the sodium azide. The dilute gas mixture is itself extremely sensitive to shock or rise of temperature, the explosion being accompanied by a flash of livid blue light whilst the glass parts of the apparatus are reduced to powder.

The analysis was therefore performed indirectly as follows: Pure carbon dioxide, generated by the action of boiled-out hydrochloric acid on calcite, was washed with sodium bicarbonate and dried by sulphuric acid and phosphorus pentoxide, and was used to carry bromine vapour (derived from the liquid at 5°) over a large surface of sodium azide, contained in a glass tube 175 cm. long and 0.5 cm. in diameter, coiled into a spiral and kept at 0° . The gas current was adjusted to carry about 0.05 g. of bromine over the azide per hour. The pale yellow gas so obtained was passed through a hard glass tube, 10 cm. long, packed with glass fragments and heated at the far end by a small bunsen flame. By this means, the compound was decomposed without explosion and the gas acquired the much darker red colour characteristic of bromine vapour. The products of decomposition were passed over silver leaf into a potash nitrometer, the carbon dioxide stream being stopped when the volume of gas in the latter had remained constant for $\frac{1}{2}$ hour. The volume of this gas, which was pure nitrogen having the normal density, was measured over water and reduced to that at N.T.P. The excess of silver leaf was dissolved in nitric acid and the silver bromide determined gravimetrically. The results are tabulated below.

| TABLE | I |
|---------------|---|
| T . T D L D L | |

| Expt. No. | Duration in hours. | Bromine taken (g.). | Bromine recovered (g. | C.c. of N_2), obtained. | $N_3: Br_a$. |
|--------------|-----------------------|------------------------|--------------------------|----------------------------|---------------|
| 1 | 2 | 0.1684 | 0.1247 | 37.07 | 1.41 |
| 2 | $5\frac{1}{2}$ | 0.3938 | 0.2128 | $74 \cdot 10$ | 1.26 |
| 3 | $2\frac{1}{2}$ | | 0.1549 | 57.60 | 1.13 |
| 4 | $4\frac{1}{2}$ | 0.1932 | 0.09447 | 36.00 | 1.11 |
| 5 | $6\frac{1}{2}$ | 0.1201 | 0.0802 | $28 \cdot 80$ | 1.14 |
| 6 | $9\frac{1}{2}$ | 0.2906 | 0.1324 | 50.00 | 1.13 |
| 7 | $10\bar{3}$ | 0.3833 | 0.1706 | 61.65 | 1.15 |

Excluding the results of experiments 1 and 2, in which the bromine vapour was in contact with the azide for a comparatively short period, the mean value is $N_3 : Br_{1:13}$.

Whilst pointing to the presence of bromoazoimide, N_3Br , the analyses show that there is about 8% more bromine in the gas than is required by the simple formula. Since the quantity of bromine recovered agrees with that required by the equation $NaN_3 + Br_2 = NaBr + N_3Br$, it was at first thought that this excess was due to a deficiency in the volume of nitrogen obtained, but the density, viscosity and chemical behaviour of the nitrogen were normal and therefore it is improbable that any polymeric modification was present, even if it could have survived the heating. A second possibility was that the reaction was reversible or incomplete, but alterations in the temperature of the reaction tube, and of the time of contact of the bromine with the sodium azide, did not materially affect the final analysis. The formation of some other nitrogen bromide, *e.g.*, NBr₃, was a third possibility.

By using a fine capillary tube as connecting link between the reaction tube and condensing vessels, any explosion could be localised, and, by immersing these vessels in freezing mixtures kept in unsilvered Dewar flasks standing in large beakers of water, rendered less dangerous. It then became possible to freeze the substance

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out, and to fractionate it by passing a stream of nitrogen over the surface whilst allowing the temperature to rise.

The analysis of these fractions was carried out as follows: The vapour derived from each fraction was absorbed in standardised solutions of carbonate-free caustic soda containing hydrogen peroxide. With this mixture the compound forms sodium azide and sodium bromide, the hydrogen peroxide reducing the sodium hypobromite first formed :

$$\begin{split} \mathbf{N_3Br} + \mathbf{2NaOH} &= \mathbf{NaBrO} + \mathbf{NaN_3} + \mathbf{H_2O}.\\ \mathbf{NaBrO} + \mathbf{H_2O_2} &= \mathbf{NaBr} + \mathbf{H_2O} + \mathbf{O_2}. \end{split}$$

By titrating the excess of sodium hydroxide with N/10-sulphuric acid and phenolphthalein, the amount of alkali required to combine with the N₃ and Br radicals was found. A known excess of silver nitrate was then added, silver bromide and azide being precipitated. The mixture was boiled with nitric acid until all the silver azide had been decomposed and the hydrazoic acid driven off. The cooled solution was titrated with ammonium thiocyanate, giving a measure of the silver nitrate required to precipitate the bromide present.*

The results are summarised in Table II.

TABLE II.

| | | | | | N_3 : Br_{L} . |
|----------|----------------|---------------|---------------|---------------|--------------------|
| Expt. | Fraction. | a. | ь. | t. | x. |
| ī | \mathbf{lst} | 91.80 | 48.30 | -10° | 1.06 |
| | 2nd | 84·7 0 | 43·7 0 | + 5 | 1.07 |
| 2 | 1st | 117.9 | 58.06 | -18 | 0.97 |
| | 2nd | 58.55 | 32.71 | + 5 | 1.26 |
| 3 | lst | 29.04 | 14.73 | -20 | 1.036 |
| | 2nd | 52.17 | $27 \cdot 19$ | -10 | 1.09 |
| | 3rd | 90.51 | 50.67 | + 5 | 1.18 |

a = c.c. of N/10-NaOH neutralised = $N_3 + Br$; b = c.c. of N/10-AgNO₃ required to neutralise Br; t = temperature below

* The above procedure provides a method for the estimation of soluble azides in presence of halides which has decided advantages over the gravimetric determination (Dennis and Isham, J. Amer. Chem. Soc., 1907, 29, 18). Owing to the number of operations involved, and the appreciable solubility of silver azide at normal temperatures, the latter method is tedious and liable to error, the results being usually low. On the other hand, the volumetric method-titration with silver nitrate followed by treatment with nitric acid and thiocyanate-is both rapid and trustworthy if the solution is first rendered barely acid by the addition of sodium acetate and acetic acid. If potassium arsenate is used as indicator in the first titration, the final acid solution is colourless. The colour of silver arsenate is, however, not so intense as that of the chromate, and quite accurate results may be obtained with the latter. Owing to the solution being slightly acid with acetic acid, a small amount of dichromate is formed and the solution is of a vellow-orange colour rather than the usual bright yellow, and the use of a comparison basin is advisable.

which the fraction was obtained. C.c. of N/10-NaOH equivalent to $N_3 = a - b$.

The first fractions (with a mean value of N_3 : $Br_{1\cdot02}$) were dark orange-red liquids which solidified at about -45° to dark red solids. The later fractions were ruby red, but even these were distinctly lighter and apparently much more mobile than liquid bromine.

If the high bromine content is due to the presence of free bromine, it should be possible to remove this by treating the liquid with sodium azide. A first fraction, obtained at -15° , was distilled on to sodium azide kept at -25° . The colour of the liquid was not altered, even after 3 hours' contact (Found : N_3 : $Br_{1.04}$). Also when gas derived directly from the apparatus and of approximate composition N₃Br_{1·13} (see Table I) was condensed on to sodium azide, and, after 3 hours, the liquid was allowed to vaporise, the proportions were N_3 : $Br_{1\cdot 16}$. The excess of bromine, therefore, is not present in the free state and the most probable explanation is that it is in the form of nitrogen tribromide, NBr₂. When the gas was passed into water the solution contained, in addition to hydrazoic and hypobromous acids, traces of ammonium salts. This cannot, however, be taken as a proof of the presence of NBr₃, for Hantzsch states that iodoazoimide (triazo iodide) gives rise to a small quantity of ammonia on hydrolysis (compare L. Spiegel, "Der Stickstoff," 1903, pp. 35, 36)."

Hantzsch (*Ber.*, 1900, **33**, 522), by the interaction of silver azide (but not potassium azide) and iodine in ether solution at 0° and evaporation of the ether, obtained red crystals of the highly unstable iodoazoimide, $N_{s}I$ (which he states is probably colourless when pure). A freshly prepared aqueous solution is neutral towards litmus and starch, but hydrolyses fairly rapidly to hydrazoic and hypoiodous acids. In non-aqueous solvents, the compound slowly decomposes to iodine and nitrogen.

When either sodium or silver azide is treated with bromine dissolved in ether, benzene, or ligroin, bromoazoimide is formed, but the method is not a convenient one. The bromine attacks the solvent to a certain extent and, owing to the great solubility and volatility of bromoazoimide, it is impossible to separate it from the solvent. Moreover, the presence of traces of water results in the immediate hydrolysis of the compound to hydrazoic and hypobromous acids. This is most striking in the case of silver azide-bromine mixtures, as the admission of a drop of water results in a vigorous evolution of nitrogen due to the rapid reaction of the hypobromous acid at once produced, with the silver azide.

Properties of Bromoazoimide.—The purest sample of the bromide obtained in these experiments was a mobile, very volatile, orange-

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red liquid, which changed to a dark red solid at about -45° . The pungent vapour has toxicological properties similar to hydrazoic acid, causing giddiness, headache, and a slackening of the muscles when inhaled. Traces of the vapour irritate the eyes and cause a slight difficulty in breathing, due apparently to congestion of the nasal mucous membrane.

Solid, liquid, and vapour are as sensitive to shock as iodoazoimide, the explosion (often apparently spontaneous) being accompanied by a flash of livid blue light. Some idea of the instability of the compound, even at -200° , may be gathered from the fact that, of twenty-four attempts at freezing the compound and determining its melting point, only six were completed without explosion. Fortunately, in the majority of cases, the sphere of action was limited to a radius of about 3 feet. Within this radius, all glass apparatus was reduced to powder; beyond it, a reinforced glass screen proved a sufficient protection. The liquid explodes in contact with phosphorus, arsenic, sodium, and silver foil, but the vapour, when diluted with nitrogen and passed over silver leaf or sodium, gives a film of the corresponding azide and bromide.

The liquid is apparently miscible in all proportions with ether, but is less soluble in benzene or ligroin. These solutions are stable for a few hours in the dark, but, when concentrated, are liable to explode on shaking, and on standing gradually decompose, giving nitrogen and bromine, the latter attacking the solvent. When passed into water, bromoazoimide hydrolyses instantaneously, giving a mixture of hydrazoic and hypobromous acids, and the solution, on standing, evolves nitrogen by the interaction of these acids. When bromoazoimide is passed into potassium iodide solution, iodine is liberated equivalent to the hypobromous acid produced and potassium azide is obtained :

$$N_3Br + 2KI = KN_3 + KBr + I_2.$$

This experiment was performed by substituting a potassium iodide absorption vessel for the heated glass decomposition tube in the apparatus described on p. 216, and it is possibly significant that 6 c.c. of nitrogen collected in the nitrometer. Some of this nitrogen may have been due to a slight decomposition of the bromoazoimide into its elements before it reached the absorption vessel, but in view of the fact that no free bromine was detected when the compound was distilled on to sodium azide (p. 219), this does not seem probable. It is thought, therefore, that the nitrogen may have been derived from NBr₃ present.

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Since bromoazoimide is instantly hydrolysed by water, the reaction in aqueous solution between bromine and sodium azide should yield hydrazoic and hypobromous acids, and therefore should differ from that between iodine and sodium or potassium azide, which occurs only in presence of sulphur compounds, yielding nitrogen (Raschig, *Chem. Ztg.*, 1908, **32**, 1203; Browne, *J. Amer. Chem. Soc.*, 1922, **44**, 2106).

When sodium azide solution was added to N/10-bromine water, the colour of the mixture faded at once to a pale straw-yellow and nitrogen was evolved at a rate depending on the concentration, temperature, and proportions of the solutions. Approximately



94% of the expected volume of nitrogen was evolved in 15 hours from concentrated solutions at the ordinary temperature. The gas was contaminated with oxygen, hydrazoic acid, and hypobromous acid.

The course of the reaction with various proportions and concentrations of the reactants can conveniently be followed by plotting the fall in iodine value of the solution against time.

Aliquot portions of the effervescing solution, removed at fixed intervals, were added to potassium iodide, and the iodine liberated by the hypobromous acid was titrated with N/10-sodium arsenite (thiosulphate is unsuitable, as it causes an instantaneous liberation of all the available nitrogen. Browne, *loc. cit.*).

In the figure, typical curves obtained with N/10-solutions at 15° are plotted.

Hypobromous acid reacts somewhat slowly with hydrazoic acid,

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but rapidly with sodium azide solutions (the latter are always alkaline by hydrolysis, and sodium hypobromite is dissociated to a greater extent than hypobromous acid). Curves 1 and 2 correspond therefore to the slow fall in concentration of hypobromous acid with hydrazoic acid, and curves 3 and 4 to the fall in the presence of an excess of sodium azide.

An abrupt change in the slope of the curves occurs when one uses more than one equivalent of sodium azide to two of bromine.

| $\operatorname{NaN}_3 + \operatorname{Br}_2 + \operatorname{H}_2 O = \operatorname{NaBr} + \operatorname{HN}_3 + \operatorname{HBr} O$ | • | • | (1) |
|--|---|---|-----|
| $HBrO + 2HN_3 = HBr + H_2O + 3N_2 \qquad .$ | • | • | (2) |

Since one equivalent of hypobromous acid can decompose two equivalents of hydrazoic acid, there is, in the solution, sufficient hypobromous acid to decompose a further equivalent of sodium azide :—

$$HBrO + 2NaN_3 = NaBr + NaOH + 3N_2 \quad . \quad . \quad . \quad (3)$$

Equivalent proportions of sodium azide solution and bromine water were mixed. After 17 hours, gas evolution had ceased and the solution was colourless and exactly neutral :----

$$\begin{split} \mathrm{NaN}_3 + \mathrm{Br}_2 + \mathrm{H}_2\mathrm{O} &= \mathrm{NaBr} + \mathrm{HBrO} + \mathrm{HN}_3 & . & . & (1)\\ \mathrm{NaN}_3 + \mathrm{HBrO} + \mathrm{HN}_3 &= \mathrm{NaBr} + \mathrm{H}_2\mathrm{O} + 3\mathrm{N}_2 & . & . & (4) \end{split}$$

One equivalent of sodium azide was mixed with two equivalents of bromine water. The effervescence was much slower, resembling that obtained when mixtures of hydrazoic and hypobromous acids react in presence of sodium bromide.

| $\mathrm{NaN}_3 + \mathrm{Br}_2 + \mathrm{H}_2\mathrm{O} = \mathrm{NaBr} + \mathrm{HBrO} + \mathrm{HN}_3$ | | • | (1) |
|---|---|---|-----|
| $HN_3 + \frac{1}{2}HBrO = \frac{1}{2}HBr + \frac{1}{2}H_2O + 1\frac{1}{2}N_2$. | • | • | (2) |

The solution should therefore contain equal parts of hydrobromic and hypobromous acids amounting to one equivalent at the conclusion of the experiment.

The nitrogen evolved would be expected to carry away the greater part of these volatile acids and yet, after 17 hours, the solution still contained a little more than a quarter of an equivalent of acid, one-half of which consisted of hypobromous acid, the other half being presumably hydrobromic acid, since there was only the slightest trace of azoimide.

The Reaction between Bromine Water and Silver Azide.—Silver azide, precipitated from a solution of sodium azide slightly acidified with nitric acid, was washed until free from soluble silver salts and treated with freshly-prepared bromine water. A vigorous

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reaction took place and silver bromide was obtained (in daylight, the yellow precipitate at once commenced to turn slate-blue unless excess of bromine was present). The evolved gas contained traces of azoimide together with about 1% of oxygen, but no nitrogen oxides, and after drying with lime and phosphorus pentoxide, had the density of ordinary nitrogen.

About 92% of the nitrogen expected from the equation $2AgN_3 + Br_2 = 2AgBr + 3N_2$ was obtained within 10 minutes of the mixing, but the presence of hydrazoic acid and oxygen suggests that the side reaction $AgN_3 + Br_2 = AgBr + N_3Br$ probably occurs in a manner analogous to the formation of iodoazoimide (Hantzsch, *loc. cit.*). The bromoazoimide was instantly hydrolysed by the water, the oxygen being derived by decomposition of the hypobromous acid thus produced (compare Fleury, *Compt. rend.*, 1920, **171**, 957). The formation of hydrazoic acid in this manner accounts for the deficiency in nitrogen, as azoimide is only slowly attacked by hypobromous acid; the latter moreover reacts very rapidly with silver azide.

Summary.

In the absence of water, bromine reacts with sodium and silver azides to give the highly unstable bromoazoimide :

$$XN_3 + Br_2 = XBr + N_3Br.$$

This compound (m. p. about -45°), whilst resembling iodoazoimide in its general properties, differs in its greater volatility and immediate decomposition by water.

Bromine water reacts instantly with sodium azide solutions to give a mixture of hydrazoic and hypobromous acids, which then interact to produce nitrogen. When the sodium azide is present in larger quantities than are required by the equation $NaN_3 + Br_2 + H_2O = NaBr + HN_3 + HBrO$, the nitrogen evolution is more rapid owing to the interaction of the hypobromous acid with the excess of sodium azide, and it is for this reason that two equivalents of bromine are able to decompose two equivalents of sodium azide.

The reaction between silver azide and bromine water differs from that with iodine solutions in that it is better represented by the equation

$$2 \text{AgN}_3 + \text{Br}_2 = 2 \text{AgBr} + 3 \text{N}_2$$

The only evidence for the momentary existence of bromoazoimide in aqueous solution is the formation of a certain amount of azoimide with consequent loss of free nitrogen.

The density or viscosity of all nitrogen samples was determined,

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but no indication of the existence of the polymeride N_3 was obtained.

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