290. *The Radiation Chemistry of Azide Solutions. Part I. The Action of* X-*Rays* (200 kv) *on Deærated Aqueous Solutions of Sodium Azide.*

By P. Kelly and M. Smith.

The principal products produced in the radiolysis (200 kv *X*-rays) of aqueous solutions of sodium azide at pH 8·0, in the absence of oxygen, are nitrogen and ammonia, the yields of which vary markedly with the azide concentration.

The results have been shown to be accommodated by a mechanism in which both the oxidising and the reducing species produced by the interaction of the ionising radiation with water react with the azide ion, leading to the N_3 radical and to nitrogen and the NH^- ion, respectively. The N_3 radical has been found to be stable with respect to its self-dissociation.

Investigations on the chemical effects of ionising radiations in deærated dilute aqueous solutions have mainly been confined to acidic solutions (pH 0—2·5). It has been found[1] that a satisfactory account of both organic and inorganic systems, in this pH range, can be given on the basis of the two primary processes:

$$H_2O \longrightarrow H + OH \qquad (1)$$

$$2H_2O \longrightarrow H_2 + H_2O_2 \qquad (2)$$

As the pH is increased, however, the hydrogen yields from organic solute systems decrease markedly,[2] as is not expected in terms of reactions (1) and (2).

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[1] Allen, *Radiation Res.*, 1954, **1**, 85.

[2] Jayson, Scholes, and Weiss, *J.*, 1957, 1358.

After a theoretical discussion by Weiss,[3] Hayon and Weiss,[4] and Weiss [5] produced some evidence that the H_2O^+ and particularly H_2O^-, formed in the primary process by the ionising radiations, may under suitable conditions be sufficiently stable to enter directly into chemical reactions. Particular interest attaches to what is denoted as the H_2O^- ion, the "polaron," *i.e.*, an electron moving around in the water accompanied by its cloud of polarisation.[3] In the following, this is written as H_2O^-, which denotes here a "polaron" and not a negatively charged water molecule.

On this basis the formation of hydrogen atoms is due to:

$$H_2O^- + H_3O^+ \longrightarrow H + 2H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

This reaction leads to pH-dependence of the hydrogen yield if a suitable solute is present to accept the H_2O^-. Allan and Scholes [6] have given a quantitative account of the pH-dependence of the radiolysis of aqueous propan-2-ol, in terms of reaction (3). Studies of the radiolysis of aqueous solutions of methanol and ethanol [7] also indicate the validity of reaction (3). We show now that the azide ion is a suitable inorganic solute capable of accepting this polaron. In the following paper, confirmation of this is obtained in a study of the irradiation of mixtures of sodium azide and various organic compounds.

RESULTS

In order to avoid the presence of hydrazoic acid [8] ($K \sim 2 \times 10^{-5}$) all experiments were carried out at pH 8·0. This was satisfactory, for (*a*) no loss of sodium azide occurred during the evacuation, (*b*) no hydrazoic acid was detectable, after irradiation, in the gas-phase products, and (*c*) the yields were independent of the buffer concentration.

Solutions of 10^{-3}M- and 10^{-1}M-sodium azide were irradiated *in vacuo* with various doses and tested for ammonia, hydrazine, hydrogen peroxide, nitrite, nitrate, and hydroxylamine. The only gaseous products detectable were nitrogen, hydrogen, and nitrous oxide.

With 10^{-3}M-sodium azide the only detectable products in solution were ammonia and nitrite, but the yield of nitrite was virtually negligible ($G \sim 0{\cdot}02$) as was that of nitrous oxide ($G \sim 0{\cdot}003$). Up to total doses of 6×10^{-6} ev/*N* per ml., the yields of ammonia, nitrogen, and hydrogen were linear functions of dose, namely, $G(N_2) = 4{\cdot}4$, $G(NH_3) = 0{\cdot}65$, $G(H_2) = 0{\cdot}7$ (Table 1). The depletion in azide over the same range of dose was also found to be a linear function of dose, with $-G(N_3^-) = 3{\cdot}1$, in agreement with the values of $G(N_2)$ and $G(NH_3)$.

TABLE 1. *Dependence on azide concentration of the initial yields of products in the irradiation of deaerated solutions of sodium azide with* X-*rays* (200 kv).

	Yields (*G* values) of				
Azide concn. (M)	N_2	H_2	N_2O	NH_3	Azide depletion
1·0	12·5	0·5	0·4	2·9	—
0·5	11·3	0·55	0·35	2·7	—
0·25	10·9	0·60	0·30	2·4	—
0·1	10·2	0·60	0·20	2·0	—
0·01	6·9	0·70	0·01	1·0	—
0·001	4·4	0·70	Negligible	0·65	3·1
Average % deviation from mean *G* value..................	±2	±2	±5	±7	±6

With 10^{-1}M-sodium azide the products in solution were again only ammonia and nitrite although the yield of both was considerably increased: $G(NH_3) = 2{\cdot}0$, $G(NO_2^-) = 0{\cdot}1$.

The initial yields of nitrogen, hydrogen, nitrous oxide, and ammonia were measured at

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[3] Weiss, *Ann. Rev. Phys. Chem.*, 1953, **4**, 143; *Experientia*, 1956, XII/7, 280.

[4] Hayon and Weiss, Proc. 2nd Internat. Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958.

[5] Weiss, *Nature*, 1960, **186**, 751.

[6] Allan and Scholes, *Nature*, 1960, **187**, 218.

[7] Lyon, Nixon, Scholes, and Smith, unpublished results.

[8] Yui, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1941, **20**, 390.

various concentrations of azide. (" Initial yields " is a somewhat arbitrary term and here represents yields for total doses in the range 0·8—3·5 × 10^{-6} ev/*N* per ml., this dose range being chosen because it represents the practical limits of detection of ammonia.) The difficulties of separation of hydroxylamine and nitrate were such that, in this initial yield dose range, a

FIG. 1. *Dependence on azide concentration of the initial yields of nitrogen in the irradiation of deaerated aqueous solutions of sodium azide with* X-*rays* (200 kv).

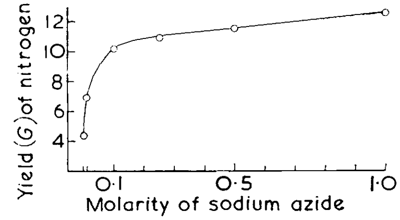


FIG. 2. *Dependence on azide concentration of the initial yields of ammonia in the irradiation of deaerated solutions of sodium azide with* X-*rays* (200 kv.)

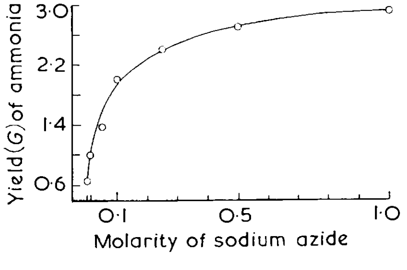


FIG. 3. *Dependence on azide concentration of the initial yields of nitrous oxide in the irradiation of deaerated aqueous solutions of sodium azide with* X-*rays* (200 kv).

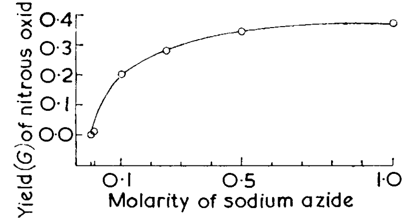
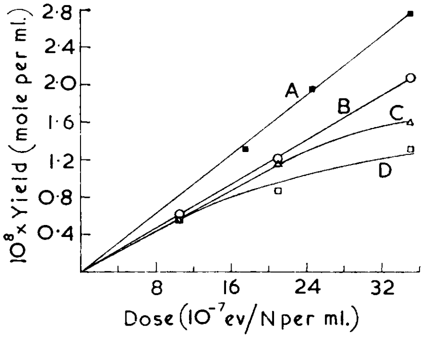


FIG. 4. *Formation of ammonia* (A), *hydrogen* (B), *nitrous oxide* (C), *and oxygen* (D) *in the irradiation of deaerated aqueous solutions of sodium azide* (10^{-1}M) *in the presence of hydrogen peroxide* (10^{-4}M) *with* X-*rays* (200 kv).



negative test did not preclude their formation up to a value of *G* ~ 0·2. In all cases the dose-yield curves were linear and the results in Figs. 1—3 are the mean values of at least three separate experiments.

Irradiations were also carried out in the presence of oxygen, at 10^{-3}M-azide only. Hydrogen peroxide was the only measurable product in solution. The dose–yield curves for the depletion of azide and the production of hydrogen peroxide, in oxygen-saturated solutions, were linear up to doses of 14 × 10^{-6} ev/*N* per ml., giving $-G(N_3^-) = 0·9 \pm 0·1$, and $G(H_2O_2) = 0·9 \pm 0·1$.

TABLE 2. *Dependence on azide concentration of the initial yields of products in the irradiation of deaerated solutions of sodium azide in the presence of hydrogen peroxide* (10^{-4}M) *with* X-*rays* (200 kv).

	Yield (*G* values) of					Depletion
Azide concn. (M)	N_2	H_2	N_2O	O_2	NH_3	of H_2O_2
0·1	5·4	0·6	0·6	0·54	0·8	2·1
0·05	4·5	0·6	0·55	0·50	0·4	2·2
0·01	—	—	—	—	0·1	2·2
0·001	3·0	0·7	0·4	0·95	0·0	2·4
Average % deviation from mean *G* value	±2	±2	±5	±5	±7	±5

A few examinations were made of those gas-phase products which were condensable in liquid oxygen: the only detectable product was nitrous oxide to an extent of $G \sim 0{\cdot}2$.

The presence of 10^{-4}M-hydrogen peroxide in the irradiation of 10^{-1}M-azide decreased the yield of nitrogen [$G(N_2) = 5{\cdot}4$] and ammonia [$G(NH_3) = 0{\cdot}8$], increased that of nitrous oxide, and led to a new product, *viz.*, oxygen (Fig. 4). Similar results were obtained at other azide concentrations (Table 2).

DISCUSSION

In view of the results of the alcohol studies mentioned above, the primary chemical processes will be taken as reaction (2) (the " molecular yield " process) and reaction (4):

$$2H_2O \longrightarrow H_2O^+ + H_2O^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

These studies also suggested that a certain number of water molecules are decomposed directly to hydrogen atoms and hydroxyl radicals, throughout the pH range; so reaction (1) will be retained to represent these.

With oxygenated solutions both hydrogen atoms and H_2O^- react with oxygen to give the same product, thus the " G(H) " value obtained is the sum of G(H) and $G(H_2O^-)$. The best value for " G(H) " appears[9] to be 2·8 and as G(H) from the alcohol studies is 0·5 (this value is for γ-rays and for the present it will be assumed that X-rays give the same), this gives $G(H_2O^-)$ 2·3. From the discussion that follows it will be seen that both hydrogen atoms and H_2O^- seem to react with the azide ion in the same manner, so it appears irrelevant here to distinguish between them. However, in Part II it will be shown that they may be differentiated by irradiating sodium azide in the presence of a second solute, such as methanol. The " molecular yields " have been taken as $G(H_2) \sim 0{\cdot}6$,[10] and $G(H_2O_2) \sim 0{\cdot}8$. The last value is a somewhat arbitrary choice. Collinson *et al.*[11] found the limiting value for $G(H_2O_2)$ to be 1·0, but that it was very dependent upon the solute concentration. The value of $G \sim 0{\cdot}8$ was chosen so that this variation might be accommodated to some extent. These values for G(H), $G(H_2O^-)$, $G(H_2)$, and $G(H_2O_2)$ give, on stoicheiometric balance of water decomposition, a value for G(OH) of 2·4.

In order to account for the above results in terms of these primary processes it has been found necessary to consider the following reactions:

$$OH + N_3^- \longrightarrow N_3 + OH^- \quad (5)$$

$$H_2O^- + N_3^- \longrightarrow N_2 + NH^- + OH^- \quad (6)$$

$$H + N_3^- \longrightarrow N_2 + NH^- \quad (6a)$$

$$H_2O^- + H_2O_2 \longrightarrow OH + OH^- + H_2O \quad (7)$$

$$H_2O^- + N_3 \longrightarrow N_3^- + H_2O \quad (8)$$

$$H + N_3 \longrightarrow (HN_3) \rightleftharpoons N_3^- + H^+ \quad (8a)$$

$$2N_3 \longrightarrow 3N_2 \quad (9)$$

$$NH^- + H_2O \longrightarrow NH_2 + OH^- \quad (10)$$

$$NH_2 + N_3^- \longrightarrow NH_2^- + N_3 \quad (11)$$

$$NH_2 + H_2O^- \longrightarrow NH_2^- + H_2O \quad (12)$$

$$NH_2 + H \longrightarrow NH_3 \quad (12a)$$

$$NH_2^- + H_2O \longrightarrow NH_3 + OH^- \quad (13)$$

$$N_3 + H_2O_2 \longrightarrow N_2 + NOH + OH \quad (14)$$

$$2NOH \longrightarrow N_2O + H_2O \quad (15)$$

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[9] Allen and Schwarz, ref. 4, in the press.

[10] Johnson and Weiss, *Proc. Roy. Soc.*, 1957, *A*, **240**, 189.

[11] Collinson, Dainton, and McNaughton, *Trans. Faraday Soc.*, 1957, **53**, 357.

The azide ion has many properties in common with the halide ions and it has been suggested[12] that its electron affinity lies between those of the bromide and the chloride ion. If the N_3 radical is stable with respect to self-dissociation, then it will also have properties lying between those of the chlorine and the bromine atom. On this basis, reactions (5), (8), (8*a*), and (9) are plausible. From other studies, reaction (7) has been found to occur rapidly. Reactions (10) and (13) are to be expected on energetic grounds and have already been suggested by Heal.[13] Reaction (11) is considered feasible, as NH_2 is isoelectronic with the hydroxyl radical. Reaction (15) seems the most likely route of formation of nitrous oxide,[14] and reaction (14) is favourable energetically.[15] Reaction (12*a*) has been found in the photolysis of ammonia.[16] Equation (6) is merely a formal representation of the stoicheiometry of the polaron–azide ion reaction, and it is not to be taken as indicating the actual mechanism.

Reaction at Low Azide Concentrations (10^{-3}M) —It is assumed that the polaron reacts very much faster with hydrogen peroxide than with the azide ion. Consequently, at low azide concentrations, the molecular yield of hydrogen peroxide (G 0·8) is removed *via* reaction (7). The hydroxyl radical [G(OH) 2·4] is thought to react *via* (5), and likewise the hydroxyl radicals (G 0·8) formed by reaction (7).

$G(NH_3) = 0{\cdot}65$, and it is believed that reactions (6), (6*a*), followed by (12), (12*a*) are responsible for this. The rest of the polaron and hydrogen-atom yield (G 0·7) {G 2·8 − G 0·8 [the polarons and hydrogen atoms utilised in (7)] − G 1·3 (those responsible for ammonia production)} is assumed to be removed by the back reaction (8), (8*a*).

The N_3 radicals are assumed to be stable with respect to self-dissociation, so that those formed in the above reaction sequences yield nitrogen *via* (9). The total nitrogen yield is then:

$$G(N_2) = 2{\cdot}4N_3\ (5) + 0{\cdot}8N_3\ [(7)\text{ followed by }(5)] + 0{\cdot}65N_2\ (6) - 0{\cdot}7N_3\ (8) = 4{\cdot}4N_2$$

(The numbers in parentheses represent the reactions responsible for production of nitrogen or the N_3 radical.) This value agrees with the experimental figure of $G(N_2) = 4{\cdot}4$, and the above sequence of reactions is also in agreement with the absence of any products other than nitrogen and ammonia.

The hydrogen yield ($G = 0{\cdot}70$) is sufficiently close to the molecular yield to be taken as such. In fact, the hydrogen yields at all concentrations are close to the molecular yields. The decrease to values below the molecular yield at the higher concentrations is similar to that found with other inorganic solutes. Following Schwartz,[17] we ascribe this to the scavenging by the azide ion of the species from the tracks responsible for the molecular yield hydrogen formation.

Reactions at High Azide Concentrations (1·0M).—At this concentration it is assumed that all the H_2O^- and hydrogen atoms react *via* (6) and that all the NH^- is consumed *via* (10), (11), and (13). The hydrogen produced at this azide concentration is less than the accepted molecular yield value, so the deficit is taken as reacting *via* (6). Thus $G(NH_3)$ from reactions (6), (10), and (11) should be $2{\cdot}8 + 0{\cdot}2 = 3{\cdot}0$.

The " molecular yield " hydrogen peroxide is presumed to be removed by reaction (14), thus $G(N_2O)$ should be 0·4. All the N_3 radicals produced in the above reaction sequence, other than those which participate in the hydrogen peroxide reaction (14), are assumed to lead to nitrogen *via* (9). According to this scheme the total nitrogen yield should be:

$$G(N_2) = 2{\cdot}4N_3\ (5) + 3{\cdot}0N_2\ (6) + 3{\cdot}0N_3\ (10, 11) + 0{\cdot}8N_2\ (14) + 0{\cdot}8N_3\ (14, 5) - 0{\cdot}8N_3\ [N_3\text{ from (5) diverted to (14)}] = 11{\cdot}9N_2$$

[12] Weiss, *Trans. Faraday Soc.*, 1947, **43**, 119.

[13] Heal, *Canad. J. Chem.*, 1953, **31**, 1153.

[14] Sneed and Brasted, " Comprehensive Inorganic Chemistry," Van Nostrand, 1956, V, 57.

[15] Uri, *Chem. Rev.*, 1952, **50**, 441.

[16] Rollefson and Burton, " Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, 1946, p. 181.

[17] Schwarz, *J. Amer. Chem. Soc.*, 1955, **77**, 4960.

Thus the above reaction sequence agrees with the experimental figures of $G(NH_3) = 2{\cdot}9$, $G(N_2O) = 0{\cdot}4$, $G(N_2) = 12{\cdot}5$.

At the intermediate concentrations the yields will depend on the relative rates of the various reactions. It is thought likely that in 0·1M-azide, none of the H_2O^- reacts with hydrogen peroxide, the yield of ammonia being less than G 2·8 because of interaction between the NH_2 radicals and hydrogen peroxide (16):

$$NH_2 + H_2O_2 \longrightarrow \begin{cases} NH_3 + HO_2 & \quad (16a) \\ NH_2{\cdot}OH + OH & \quad (16b) \end{cases}$$

Reaction (16*b*) leads directly to a reduction in the ammonia yield. Reaction (16*a*) will also lead to a decrease in the ammonia yield, as the HO_2 will probably lead to the formation of NH_2O_2 *via* reactions (19) and (17)

$$NH_2 + O_2 \longrightarrow NH_2O_2 \quad \text{. . . . . (17)}$$

The small yield of nitrite ($G \sim 0{\cdot}1$) found at this azide concentration can be accounted for in terms of (16*a*) and (17), as NH_2O_2 is a likely precursor of nitrite.[18]

If reaction (16) is correct, then the slow increase in nitrogen and ammonia between 0·1M- and 1·0M-azide is a result of reaction (11) competing with (16). The release of hydrogen peroxide from reaction (16) then enables reaction (14) to proceed more effectively, resulting in an increase in nitrous oxide, as observed.

Reactions in the Presence of Oxygen (10^{-3}M-*Sodium Azide*).—It is seen that the presence of oxygen markedly reduces the extent of azide decomposition. As reaction (5) should proceed whether or not oxygen is present, the extent of azide depletion should be at least G 2·4. The experimental figure of G 0·9 suggests therefore that a considerable amount of back-reaction ensues, probably as:

$$H_2O^- + O_2 \longrightarrow O_2^- \quad \text{. . . . . (18)}$$

$$H + O_2 \longrightarrow HO_2 \rightleftharpoons H^+ + O_2^- \quad \text{. . . . . (18a)}$$

$$O_2^- + N_3 \longrightarrow N_3^- + O_2 \quad \text{. . . . . (19)}$$

The yield of nitrous oxide, G 0·2, found experimentally, can be accounted for in terms of reaction (14) going to an extent of a G 0·4. If a G 0·6 of hydrogen peroxide is produced *via* the reaction (20), then, on use of the same values for the water decomposition as before, this leads to a value of 0·8 for $-G(N_3^-)$ and 1·0 for $G(H_2O_2)$ which compare well with the experimental figures of $-G(N_3^-) = 0{\cdot}9$, $G(H_2O_2) = 0{\cdot}9$.

$$2O_2^- \longrightarrow O_2^{2-} + O_2 \quad \text{. . . . . (20)}$$

Some confirmation for the suggestion that the nitrous oxide is formed *via* reaction (14) was given by an experiment carried out in the presence of hydrogen peroxide (10^{-4}M) in which the nitrous oxide yield increased to G 0·44.

Reactions in the Presence of Hydrogen Peroxide.—The addition of hydrogen peroxide before the irradiation of 0·1M-azide is seen to result in a decrease in the yields of ammonia and nitrogen. At the same time the yield of nitrous oxide is considerably increased and oxygen is formed. These changes in ammonia and nitrous oxide yields would be expected on the basis of, and so lend support to, reactions (14) and (16). At lower concentrations of azide, reaction (7) would be expected to compete with (6), resulting, as found, in an absence of ammonia. However, the increased number of hydroxyl radicals, produced *via* (7), should lead to at least a slight increase in the nitrogen yield, and certainly not to a decrease as observed. The increasing yield of oxygen suggests that this is possibly due to interaction of the hydroxyl radicals with the hydrogen peroxide, as:

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \quad \text{. . . . . (21)}$$

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[18] Rigg, Scholes, and Weiss, *J.*, **1952**, **3034**.

In view of the difficulties of analysis of nitrogen–oxygen compounds, and our lack of knowledge as to their reactivity, no attempt was made to amplify these preliminary experiments.

The ultraviolet band of the azide ion is very similar to that of the iodide ion,[12] and consequently has been interpreted in terms of an electron transfer to water.[19] Unlike the case of the iodide ion, however, considerable photochemical decomposition takes place in neutral and alkaline conditions.[20] It has also been found that the hydrogen forms only 2% of the gaseous products,[21] the rest being nitrogen. It seems reasonable to suppose that these results can be ascribed to the operation of reaction (6). Further support for reaction (6) comes from the fact that sodium azide solutions are reduced by alkaline sodium amalgam,[22] the main products being nitrogen and ammonia.

EXPERIMENTAL

X-Ray irradiations were carried out by using a Victor Maximar set operating at 200 kv and 15 mA. The Pyrex irradiation vessels, incorporating a large gas space, gave dose rates in the region of $3{\cdot}5 \times 10^{-7}$ ev/*N* per ml. per min., for the 100 ml. samples normally used, as measured by the ferrous sulphate dosimeter, the value of 15·5 being used for $G(\mathrm{Fe}^{3+})$.[23]

Triply distilled water was used throughout the work, both for preparation of solutions and analysis of products. It was obtained by distilling ordinary distilled water from potassium permanganate and then from phosphoric acid.

All chemicals used were of "AnalaR" grade, with the exception of the sodium azide itself, which was purified by successive recrystallisations from triply distilled water. The sodium azide solutions were buffered at pH 8, by a 10^{-3}M Sörensen buffer.[24]

Evacuation and Gas Collection.—The apparatus used for evacuation and degassing of solutions and for collection and measurement of the gaseous products was similar to that used previously in these laboratories.[25] Satisfactory deæration was achieved by an initial evacuation followed by alternative vigorous shaking and connection to the vacuum-system for a very short period. Evacuated unirradiated solutions were subjected to the gas-collection procedure, and subsequent measurement of the gas volume confirmed the efficiency of the evacuation method.

The gaseous irradiation products were collected *via* a solid carbon dioxide–acetone trap, in a gas-burette capable of handling up to 30 c.c. of gas at S.T.P. Thorough shaking of the vessel before attachment to the collection system was not sufficient to ensure complete removal of the gas. After the first collection, a second shaking was necessary to liberate the remainder of the gas from the solution. The withdrawal of gas was effected by a Toepler pump and the procedure was monitored by a Pirani gauge. After measurement of its volume, the gas was transferred to a sample vessel for subsequent analysis by a Metropolitan-Vickers M.S.2. mass spectrometer.

Mass-spectrometric Analysis.—The gaseous products were hydrogen, nitrogen, and nitrous oxide together with carbon dioxide (present in the unirradiated solution) and small amounts of air. This mixture presented no difficulties in analysis. Conservative estimates of the accuracy of the analyses are: nitrogen ± 2·0 moles% in the presence of "air" nitrogen; hydrogen, ±0·5 mole%; and nitrous oxide, ±0·1 mole% in the presence of carbon dioxide.

Analysis of Products in Solution.—Determination of azide depletion. It was only in the region of 10^{-3}M-azide that $-G(\mathrm{N_3}^-)$ could be measured; at higher concentrations the % depletion of azide was too small to be detected. Satisfactory results were obtained by using two different methods:

(a) Ferric nitrate method. Roberson and Austin's method [26] was slightly modified for use

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[19] Smith and Symons, *Trans. Faraday Soc.*, 1958, **54**, 338.

[20] Bonnemay, *J. Chim. phys.*, 1944, **41**, 18.

[21] Kelly and Smith, unpublished results.

[22] Audrieth, *Chem. Rev.*, 1934, **15**, 169.

[23] Farmer, Rigg, and Weiss, *J.*, 1955, 582.

[24] Vogel, "Text Book of Quantitative Inorganic Analysis," Longmans, Green & Co., London, 1948, p. 809.

[25] Stein and Weiss, *J.*, 1949, 3245.

[26] Roberson and Austin, *Analyt. Chem.*, 1957, **29**, 854.

with dilute azide solutions buffered at pH 8. It was found that a more concentrated ferric nitrate solution was necessary for full colour development.

To 10 ml. of ferric solution (made by dissolving 20 g. of ferric nitrate in 100 ml. of water, then adding 5 ml. of concentrated nitric acid and making up the volume to 1 l.) were added 4 ml. of 10^{-3}M-azide solution. The volume was made up to 50 ml. and the optical density, measured after 5 min., on a Unicam S.P. 600 spectrophotometer at 460 mμ using 4-cm. cells, was 0·5.

An appropriate volume of the irradiated solution was taken, so that by the above procedure, an optical density close to 0·4 was obtained. The actual optical density was then found by comparison with the standard and the result was checked by measurement against the appropriate blank.

(b) Ceric method. The oxidation of azide ion by ceric salts is the basis of two methods of estimation of azide. The first involves measurement of the nitrogen evolved and, in the second, ferrous perchlorate is titrated against excess of ceric salt solution. These methods are not wholly suitable for dilute azide solutions.

10^{-3}M-Solutions of sodium azide were found to be immediately and quantitatively oxidised by ceric sulphate in acid solution, the extent of oxidation being followed by spectrophotometric determination of the excess of ceric sulphate. The procedure was as follows: to 10 ml. of 10^{-3}M-ceric sulphate, which had been made approximately 0·8N in sulphuric acid, were added 2 ml. of concentrated sulphuric acid and 8·5 ml. of standard 10^{-3}M-buffered azide solution. After the volume had been made up to 50 ml. the excess of ceric sulphate was measured at 315 mμ in 1-cm. cells against the reference solution. An appropriate amount of the irradiated solution, treated in the same manner, was taken so that a measurable difference in optical density was obtained.

Determination of ammonia. Ammonia was determined by Beeghly's method.[27] For 10^{-3}M-azide solutions, 25—40 ml. of irradiated solution (the amount depending upon dose received) were made up to 50 ml. after addition of 1 ml. of Nessler's reagent. Measurements were made at 410 mμ in 4-cm. cells. A calibration curve was constructed by using a standard ammonium chloride solution and this was checked at regular intervals. It was necessary to make up fresh reagent each month.

The azide ion, in concentrations greater than 10^{-3}M, interfered with development of the Nessler colour. For solutions whose optical density should have been 0·2 or less, the colour was suppressed markedly; and for more concentrated ammonia solutions, the true value was reached after varying periods of time dependent upon the azide concentration, after which the optical density continued to rise.

The time elapsing before the correct optical density was reached was found for each azide concentration studied. The procedure for determination of ammonia in irradiated solutions was then as follows: Three 25 ml. samples of the irradiated solution were placed in 50 ml. flasks. To these were added severally 4, 6, and 8 ml. of standard 10^{-4}M-ammonium chloride solution, followed by 1 ml. of Nessler's reagent and water to the mark. The optical densities were then measured after the predetermined time interval. The absorption due to the added ammonia was subtracted from these values. Unless the three results thus obtained agreed to within 5%, the determination was repeated.

Determination of nitrite. Nitrite was measured after removal of azide by precipitation as silver azide. For 0·1M-azide solutions, 20 ml. of irradiated solution were added slowly with stirring to 25 ml. of 0·1M-silver nitrate which had been heated to near the b. p. The precipitate was filtered off hot (Whatman No. 542 filter-paper) and washed with 5 ml. of water. The filtrate was made up to 50 ml. when necessary. To 10 ml. of hot silver nitrate solution were added 25 ml. of filtrate, again slowly and with stirring. The filtration and washing procedure was repeated, the final volume of the filtrate being measured. Normally, this sufficed to remove all the azide present, but a confirmatory test (10 ml. of final filtrate added to 5 ml. of hot silver nitrate solution) was always carried out. Endres and Kaufman's method [28] was applied to the final filtrate and it worked excellently for standard nitrite solutions of concentrations greater than 2×10^{-6}M. For solutions of lower azide concentration, smaller amounts of silver nitrate were used and precipitation was carried out much more slowly to ensure the formation of large particles.

[27] Beeghly, *Ind. Eng. Chem. Anal.*, 1942, **14**, 137.
[28] Endres and Kaufman, *Annalen*, 1935, **518**, 109.

Determination of hydrazine and hydroxylamine. The azide ion interfered seriously with the method for hydrazine determination suggested by Pesez and Petit; [29] and Endres and Kaufman's method for determination of hydroxylamine by conversion into nitrite could not be used owing to the immediate reaction between nitrite and azide under acid conditions. The azide was therefore removed, before the determination of these products, by passing the solutions down a column of Dowex 2 (× 10) (Cl form) ion-exchange resin (10 cm. × 3 cm.^{2}). Usually 25 ml. of the solution, followed by 25 ml. of water, were passed down the column and made up to the mark in a 50 ml. flask. Treatment of these solutions with ferric nitrate showed the absence of any appreciable amounts of azide. For 0·1M- and greater concentrations of azide, each column was used once only, and was regenerated with 2N-hydrochloric acid (2 bed volumes) followed by water (10 bed volumes).

Various synthetic mixtures of hydrazine, hydroxylamine, and azide were passed through the columns. No loss of hydrazine occurred, for azide concentrations up to 1·0M, when the final concentration of hydrazine, after colour development, was in the range 2—10 × 10^{-6}M. Hydroxylamine, where the final concentration was in the same range, gave good results with 10^{-3}M-azide, but at the higher azide concentrations some loss occurred. As no hydroxylamine could be detected in the reactions there was no necessity to rectify this.

Detection of nitrate. Nitrate was detected, after reduction with nascent hydrogen, as nitrite.[30] The azide and any nitrite initially present were removed simultaneously by acidifying with glacial acetic acid and boiling the solution. Samples from such a treatment were added to a 25 ml. flask containing 2 ml. each of sulphanilic acid and α-naphthylamine reagents, and a trace of zinc dust. A final concentration of nitrate of 5 × 10^{-6}M yielded a faint but definite pink colour.

Determination of hydrogen peroxide. This was estimated with potassium iodide; [31] no interference from the azide ion up to a concentration of 1·0M was observed. The solutions were brought to pH 4·0 by the addition of sulphuric acid, before Hochanadel's reagents were added.

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[29] Pesez and Petit, *Bull. Soc. chim. France*, 1947, 122.
[30] Feigl, " Spot Tests," Nordemann, 1937, 202.
[31] Hochanadel, *J. Phys. Chem.*, 1952, **56**, 587.