

**291.** *The Radiation Chemistry of Azide Solutions. Part II.\* The Action of X-Rays (200 kv) on Deaerated Aqueous Solutions of Sodium Azide in the Presence of Different Organic Solutes.*

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Deaerated aqueous solutions of sodium azide have been irradiated with X-rays (200 kv) in the presence of methanol, propan-2-ol, acetone, and formaldehyde. The azide-methanol solutions have been studied over a wide range of concentrations; in all cases the main reaction products were: nitrogen, ammonia, hydrogen, ethylene glycol, and formaldehyde. The results confirm the mechanism for radiolytic decomposition of the azide ion previously presented. Studies on the azide-propan-2-ol and azide-acetone systems provide confirmatory evidence for the assumption of  $\text{H}_2\text{O}^-$  (polaron) as a primary species in the radiolysis of water.

IN the preceding paper a mechanism was presented for the action of X-rays (200 kv) on deaerated aqueous solutions of sodium azide. Although this mechanism was able to give a coherent account of the dependence of the yields on concentration, postulation of several new reactions made it somewhat speculative. Studies of the radiolysis of aqueous solutions of methanol and propan-2-ol have confirmed the presence of the  $\text{H}_2\text{O}^-$  species (polaron, not an ionised water molecule) as one of the primary products of the

\* Part I, preceding paper.

radiolysis of water. It seemed likely, therefore, that the irradiation of sodium azide in the presence of these alcohols could provide further evidence for some of the reactions postulated.

*Results.*—Irradiations were carried out on solutions buffered at pH 8.0 ( $10^{-3}$ M Sørensen buffer) to avoid the presence of hydrazoic acid.

FIG. 1. Dependence on methanol concentration of the initial yields of nitrogen (A), ammonia (B), and hydrogen (C) in the irradiation of deaerated aqueous solutions of sodium azide ( $10^{-3}$ M) with X-rays (200 kv).

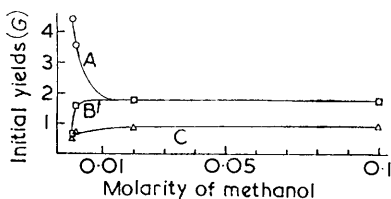


FIG. 2. Dependence on methanol concentration of the initial yields of nitrogen (A), ammonia (B) and hydrogen (C) in the irradiation of deaerated aqueous solutions of sodium azide ( $10^{-2}$ M) with X-rays (200 kv).

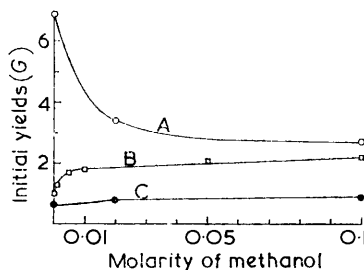


FIG. 3. Dependence on methanol concentration of the initial yields of nitrogen (A), ammonia (B), hydrogen (C), and nitrous oxide (D) in the irradiation of deaerated aqueous solutions of sodium azide ( $10^{-1}$ M) with X-rays (200 kv).

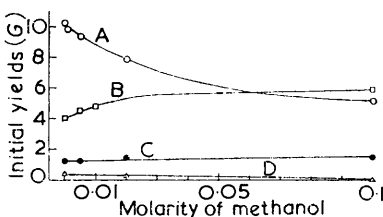


FIG. 4. Formation of acetone by irradiation of deaerated aqueous solutions of sodium azide, (A)  $5 \times 10^{-2}$ M, (B)  $10^{-2}$ M, in the presence of propan-2-ol (0.1M) with X-rays (200 kv).

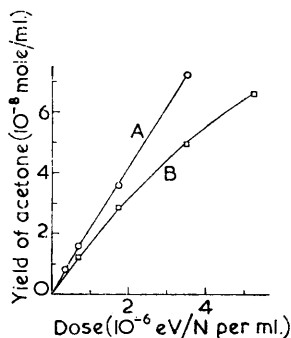


FIG. 5. Dependence on acetone concentration of the initial yields of nitrogen in the irradiation of deaerated aqueous solutions of sodium azide, (B) 0.1M, (A) 0.5M, with X-rays (200 kv).

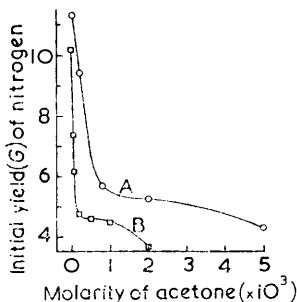
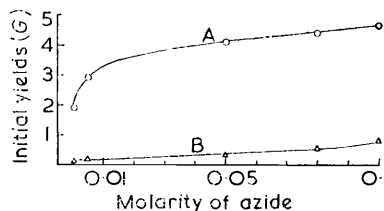


FIG. 6. Dependence on azide concentration of the initial yields of nitrogen (A) and nitrous oxide (B) in the irradiation of deaerated aqueous solutions of sodium azide in the presence of acetone ( $5 \times 10^{-4}$ M) with X-rays (200 kv).



Mixtures of methanol ( $10^{-3}$ – $10^{-1}$ M) and sodium azide ( $10^{-3}$ – $10^{-1}$ M) were irradiated with different doses. The only gaseous products were nitrogen, hydrogen, and nitrous oxide. Products tested for in solution were hydroxylamine, hydrazine, nitrite, nitrate, hydrogen

peroxide, ammonia, formaldehyde, and ethylene glycol, but only the last four of these were detected.

TABLE 1. *Dependence on the azide concentration of initial yields of products formed in the irradiation (X-rays, 200 kv) of azide solutions in the presence of methanol (10<sup>-1</sup>M and 10<sup>-3</sup>M).*

MeOH concn. (M)	Azide concn. (M)	Yields (G values)						
		N <sub>2</sub>	H <sub>2</sub>	N <sub>2</sub> O	NH <sub>3</sub>	C <sub>2</sub> H <sub>4</sub> (OH) <sub>2</sub>	CH <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>
0.1	0.1	5.05	0.72	0.03	2.8	NM	2.0	0.3
0.1	0.01	2.7	0.82	NM	2.2	1.7	1.6	0.2
0.1	0.001	1.7	0.90	0.006	1.7	2.1	0.4	0.0
0.001	0.001	3.55	0.75	NM	1.6	NM	NM	NM

NM = Not measured.

TABLE 2. *Dependence on the azide concentration of initial yields of nitrogen and hydrogen in the irradiation (X-rays, 200 kv) of azide solutions in the presence of propan-2-ol (10<sup>-1</sup>M).*

Azide concn. (M)	0.1	0.05	0.01
Yield of N <sub>2</sub>	3.0	2.5	1.52
Yield of H <sub>2</sub>	0.85	0.9	0.9

Having established the linearity of the yield-dose curves up to total doses of  $6 \times 10^6$  eV/N per ml. for the gaseous products, we investigated the variation of the initial yields of

FIG. 7. *Dependence on alcohol concentration [(A) methanol, (B) propan-2-ol] of the initial yields of nitrogen in the irradiation of deaerated aqueous solutions of sodium azide (0.1M) in the presence of acetone (5 × 10<sup>-4</sup>M) with X-rays (200 kv).*

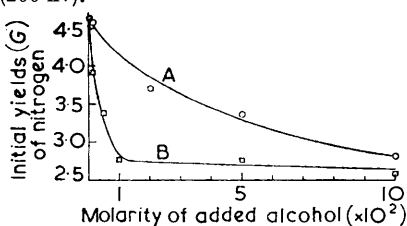
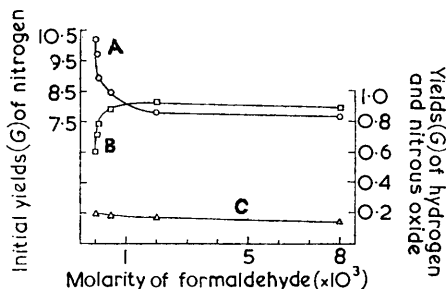


FIG. 8. *Dependence on formaldehyde concentration of the initial yields of nitrogen (A), hydrogen (B), and nitrous oxide (C) in the irradiation of deaerated solutions of sodium azide (0.1M) with X-rays (200 kv).*



nitrogen, hydrogen, ammonia, and nitrous oxide for a variety of mixtures (Figs. 1, 2, and 3). Table 1 shows the initial yields of products for varying concentrations of azide in the presence of 0.1M-methanol, and the nitrogen, hydrogen, and ammonia yields for 10<sup>-3</sup>M-azide in the presence of 10<sup>-3</sup>M-methanol.

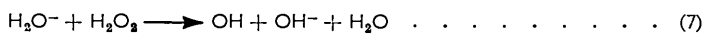
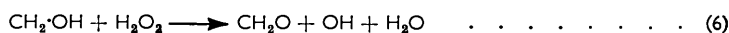
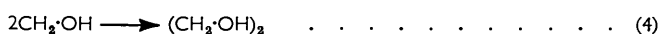
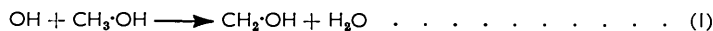
Solutions of propan-2-ol (0.1M) and sodium azide (10<sup>-2</sup>—10<sup>-1</sup>M) were irradiated with various doses. Analysis of the products in solution was carried out as for the methanol mixtures. The only measurable product was acetone. Ammonia was also formed but the acetone interfered so seriously with the Nessler colour as to make quantitative measurement impossible. The dose-yield curves for acetone are given in Fig. 4, and the initial yields of nitrogen and hydrogen appear in Table 2.

The effect of adding acetone before irradiation of sodium azide solutions was also studied. The initial yields of nitrogen for azide solutions (0.1—0.5M) at various acetone concentrations are given in Fig. 5. The dependence of the nitrogen yield on azide concentration at constant acetone concentration (5 × 10<sup>-4</sup>M) (Fig. 6) and the influence of the addition of methanol or propan-2-ol on the yield of nitrogen from 0.1M-azide solutions, in the presence of acetone (5 × 10<sup>-4</sup>M), have been studied (Fig. 7).

Fig. 8 shows the changes in the initial yields of nitrogen, hydrogen, and nitrous oxide from 0.1M-azide in the presence of varying amounts of formaldehyde.

## DISCUSSION

*Azide Solutions containing Methanol.*—Studies of the radiolysis of deaerated aqueous methanol solutions<sup>1</sup> have shown that, at pH 8·0, the same values being used for the primary water decomposition yields as given in Part I, the results can be described in terms of the following reactions:



The extent to which the  $\text{CH}_2\cdot\text{OH}$  radicals distribute themselves between the dimerisation (4) and the disproportionation (3) reaction is not known exactly but appears to be such that  $k_4/k_3 \sim 5$ . The extent of reaction (6) as compared with (3) and (4) is also not known, but it seems probable that the maximum amount of the molecular-yield hydrogen peroxide which can be removed by this reaction is  $G \sim 0\cdot3$ .

In terms of this reaction scheme the presence of methanol in the azide solutions should result in a competition between the two solutes for the hydroxyl radicals, whilst the  $\text{H}_2\text{O}^-$  would react solely with the azide ions. Interference from the back-reaction (5) might be expected to be small at low doses, in view of the value of  $k_4/k_3$ , unless the  $\text{H}_2\text{O}^-$  reacts very much faster with formaldehyde than with the azide ion, which actually is not the case (see below). In the previous paper, it was suggested that the  $\text{NH}_2$  radical reacts only slowly with the azide ion, so it seemed likely that reaction (16) would occur.

(i) In  $10^{-3}$  M-azide solutions the addition of methanol in increasing amounts is seen to lower the nitrogen yield, to a limit of  $G = 1\cdot7$ . At the same time the ammonia yield rises markedly and then also reaches a limiting value of  $G = 1\cdot7$ , whilst the hydrogen yield rises slightly and then reaches a limiting value of  $G = 0\cdot9$  (Fig. 1).

The molecular-yield hydrogen peroxide at these relatively low azide concentrations is removed *via* reaction (7) and the presence of the methanol should not alter this. The absence of hydrogen peroxide in the 0·1M-methanol solution is in agreement with this supposition.

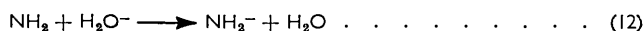
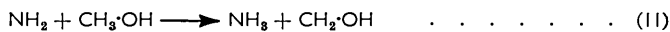
The decrease in nitrogen yield is attributed to the methanol's removing hydroxyl radicals *via* reaction (1), thus preventing reaction (9) from occurring:



The increase in the ammonia yield is thought to be due to the suppression of the back-reaction (10),



this suppression being a result of (a) the decrease in  $\text{N}_3$  radicals caused by the operation of reaction (1) in place of (9) and (b) the removal of  $\text{NH}_2$  radicals *via* reaction (11) instead of *via* (12):

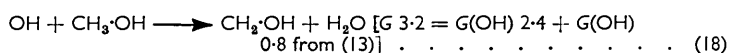
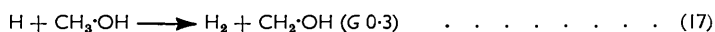
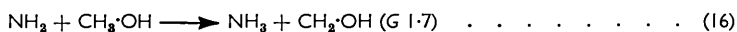
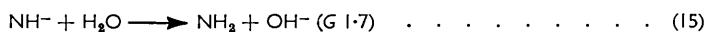
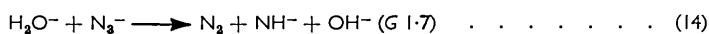
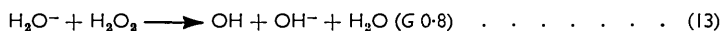


The increase in hydrogen yield seems likely to be due to the operation of reaction (2),

<sup>1</sup> Lyon, Scholes, and Smith, unpublished results.

the limiting value of  $G$  0.9, with allowance for the molecular-yield hydrogen  $G(\text{H}_2)$  0.6, leading to a value for  $G(\text{H})$  of 0.3.

The above suggestions lead to the following sequence for the results on the 0.1M-methanol solution:



This sequence clearly leads to an explanation of the results in terms of the primary water yields. Also, on the basis of this sequence, the  $\text{CH}_2\cdot\text{OH}$  radical yield should be:

$$G(\text{CH}_2\cdot\text{OH}) = 3.2 \text{ (18)} + 1.7 \text{ (16)} + 0.3 \text{ (17)} = 5.2$$

(The numbers in parentheses represent the reactions responsible for  $\text{CH}_2\cdot\text{OH}$  radical production.) The expected total yield for the aldehyde and glycol is thus  $G = 2.6$ , which is confirmed by the experimental values of  $G(\text{glycol}) = 2.1$ , and  $G(\text{formaldehyde}) = 0.4$ . (These values are also in good agreement with the value of 5 for  $k_4/k_3$ .)

At equal concentrations of methanol and azide ( $10^{-3}\text{M}$ ),  $G(\text{N}_2) = 3.55$ ,  $G(\text{NH}_3) = 1.6$ , and  $G(\text{H}_2) = 0.75$ . The decrease in ammonia and hydrogen yields as compared with those in the 0.1M-methanol solution represents a loss of  $G$  0.25 [ $G(\text{H})$  0.15 plus  $G(\text{H}_2\text{O}^-)$  0.1]. In terms of the above reactions this deficiency must result from the operation of the back-reaction (10), which is enhanced by the increased extent of reaction (9) as compared with (1). The yield of nitrogen from reaction (9) is  $G$  1.95 [ $G(\text{N}_2)$  3.55 —  $G(\text{N}_2)$  1.6 from (14)] so that, after allowance for the back-reaction ( $G$  0.25), the extent of reaction (9) must be  $G$  1.55. The total hydroxyl radical yield is  $G = 3.2$ , *i.e.*, 2.4 from  $G(\text{OH})$  plus 0.8 from reaction (13). As  $G$  1.55 of this must participate in reaction (9),  $G$  1.65 is reacting with the methanol (1), and consequently the ratio of the rate constants

$$k_{\text{OH} + \text{N}_3^-} / k_{\text{OH} + \text{CH}_3\cdot\text{OH}} = k_9 / k_{18} = 1.55 / 1.65 \sim 0.94.$$

The hydrogen yield, which is increased in the presence of methanol, does not appreciably change when the methanol concentration is increased from  $10^{-2}$  to  $10^{-1}\text{M}$ . This suggests that all the available hydrogen atoms are reacting with methanol. This limit of hydrogen is  $G(\text{H}_2) = 0.9$ ; thus with a molecular yield of 0.6, a value for  $G(\text{H}) = 0.3$  is obtained.

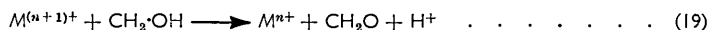
(ii) In  $10^{-2}\text{M}$ -azide solutions the addition of methanol also results in a decrease in the nitrogen yield and an increase in the ammonia and hydrogen yields. At 0.1M-methanol the ammonia yield is increased to  $G(\text{NH}_3) = 2.2$ , and that this is due to a release of  $\text{H}_2\text{O}^-$  from reaction (13) is confirmed by the appearance of hydrogen peroxide as a product.

The yield of nitrogen [ $G(\text{N}_2) = 2.7$ ] is slightly greater than that of the ammonia, and if the excess is taken as a result of reaction (9), a value for  $k_9/k_{18} \sim 0.93$  is obtained, which agrees well with the value calculated above, although some uncertainty could be involved in using the relatively small difference in the nitrogen yields. This excess represents a value of 0.3 for  $G(\text{OH})$  consumed in (9), leaving  $G(\text{OH}) = 2.1$  to react *via* (18).

The  $\text{CH}_2\cdot\text{OH}$  radical yield at  $10^{-1}\text{M}$ -methanol should be:

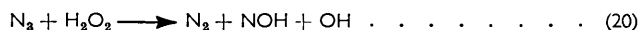
$$\begin{aligned} G(\text{CH}_2\cdot\text{OH}) &= 2.2 \text{ [from } \text{NH}_2 + \text{CH}_3\cdot\text{OH} \text{ (16) as the ammonia yield is 2.2]} \\ &+ 0.2 \text{ [from } \text{H} + \text{CH}_3\cdot\text{OH} \text{ (17) as the hydrogen yield is 0.82]} \\ &+ 0.6 \text{ [from the OH radicals produced from molecular-yield hydrogen} \\ &\quad \text{peroxide via (6) and (7) as } G(\text{H}_2\text{O}_2) \text{ is only 0.2]} \\ &+ 2.1 \text{ [from } G(\text{OH}) \text{ (18) minus those OH radicals consumed in (9)]} \\ &= 5.1 \end{aligned}$$

The aldehyde and glycol yields should thus be similar to those found in  $10^{-3}\text{M}$ -azide solutions. The experimental values were  $G(\text{glycol}) = 1.7$  and  $G(\text{aldehyde}) = 1.6$ . It is thought that this high aldehyde yield could be due to the presence of some heavy-metal impurities which might react with the  $\text{CH}_2\cdot\text{OH}$  radicals according to:



Some support for this comes from experiments on  $10^{-3}\text{M}$ -azide solutions in the presence of  $0.1\text{M}$ -methanol where the prior addition of  $10^{-6}\text{M}$ -ferric nitrate resulted in a doubling of the aldehyde yield. The source of these impurities is most likely to be sodium azide.

(iii) In  $0.1\text{M}$ -azide solutions, in the presence of  $0.1\text{M}$ -methanol, the ammonia yield is  $G(\text{NH}_3) = 2.8$ , and if this ammonia is produced by reaction of the  $\text{NH}_2$  radicals with methanol by reaction (16), then, of the yield of  $G(\text{N}_2) = 5.05$ , the proportion  $G(\text{N}_2) = 2.25$  is to be ascribed to reaction (9). This assignment is supported by the fact that it leads to a value for  $k_9/k_{18} = 1.0$ . The total hydroxyl radical yield required to obtain such a ratio was taken as  $G(\text{OH}) = 2.9$ . This value is the sum of the primary hydroxyl radical yield,  $G(\text{OH}) = 2.4$  and  $G = 0.5$  hydroxyl radicals formed from the decomposition of molecular-yield hydrogen peroxide by reaction (6) and, because a small yield of nitrous oxide is obtained by reaction (20):



The expected  $\text{CH}_2\cdot\text{OH}$  radical yield was:

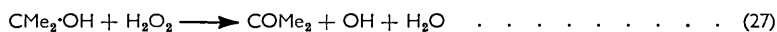
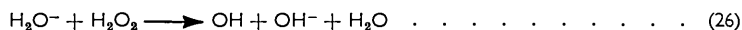
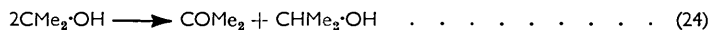
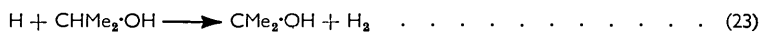
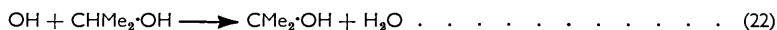
$$\begin{aligned} G(\text{CH}_2\cdot\text{OH}) &= 2.8 (16) + 0.5 [(6) \text{ and } (20) \text{ followed by } (18)] + 0.9 [(18) - (9)] \\ &= 4.2 \end{aligned}$$

The aldehyde yield was in fact  $G = 2.0$ , but no value for the glycol yield could be obtained because of the difficulties of estimating glycol in the presence of a high concentration of sodium azide. The aldehyde yield is in keeping with the supposition that the heavy-metal ion impurities come from the sodium azide used.

The decrease in the nitrogen yield, when the methanol concentration is increased, is too great to be explained in terms of a value of  $k_9/k_{18} = 1.0$ . However, if the  $\text{NH}_2$  radical reacts with the azide ion according to (21), then the added methanol should decrease the nitrogen yield produced by reaction (21) as well as (9). On this basis the decrease in nitrogen is well accounted for.



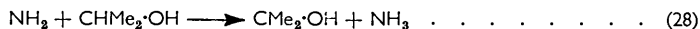
*Azide Solutions in the Presence of Propan-2-ol.*—Irradiation with  $\gamma$ -rays ( $^{60}\text{Co}$ ) of deaerated aqueous solutions of propan-2-ol leads to the formation of acetone and hydrogen.<sup>2</sup> At pH 8.0 the yields of both these products are  $G \sim 1.0$ . The following reaction sequence can account for this result:



The irradiation of solutions of azide containing propan-2-ol is seen to lead to a very large increase in the yield of acetone. This is expected in terms of reaction (14) which will

<sup>2</sup> Allan and Scholes, *Nature*, 1960, **187**, 218.

decrease the back-reaction (25) and at the same time increase the radical yield according to:



In  $10^{-2}\text{M}$ -azide solutions in the presence of  $0.1\text{M}$ -propan-2-ol there is a marked curvature in the yield-dose curve for acetone, and this suggests that  $\text{H}_2\text{O}^-$  reacts very much faster with acetone than with the azide ion. That this curvature is a result of reaction (25) is confirmed by the rather more nearly linear yield-dose curve obtained in  $5 \times 10^{-2}\text{M}$ -azide solutions. These curves both give a ratio for the rate constant ratio  $k_{25}/k_{14} \sim 10^3$ .

In  $0.1\text{M}$ -azide solutions in the presence of  $0.1\text{M}$ -propan-2-ol the yield of nitrogen  $G(\text{N}_2) = 3.0$  is less than that obtained from the corresponding solution containing methanol; hence the hydroxyl radicals must react faster with propan-2-ol than with methanol. In  $10^{-2}\text{M}$ -azide solutions in the presence of  $0.1\text{M}$ -propan-2-ol the hydrogen yield was  $G(\text{H}_2) = 0.9$ , which gives a value of  $G(\text{H}) 0.3$ , the same as with methanol.

*Azide Solutions in the Presence of Acetone.*—The ratio of the rate constants  $k_{25}/k_{14} \sim 10^3$ , deduced from the above experiments, suggested that the addition of increasing amounts of acetone to a  $0.1\text{M}$ -azide solution would result in a decrease in the nitrogen yield to a limiting value corresponding to  $\{G(\text{OH}) + G(\text{H})\}$  plus the yield of nitrogen resulting from hydrogen peroxide consumption in reactions (27) and (20). The nitrogen does indeed fall sharply to a limiting value, but at higher acetone concentrations a further decrease in the nitrogen yields occurs. The "plateau region" in which the nitrogen yield remains constant (see Fig. 5) has a value  $G(\text{N}_2) = 4.65$ , reasonably close to the calculated figure  $G(\text{N}_2) = 5.5$ . The onset of the "plateau region" corresponds to a value for the rate constant ratio  $k_{25}/k_{14} \sim 2 \times 10^3$ . Increasing the concentration to  $0.5\text{M}$ -azide results in a five-fold increase in the amount of acetone required to reach this region, confirming the existence of a competition between acetone and azide for  $\text{H}_2\text{O}^-$ . The nitrogen yield  $G(\text{N}_2) = 5.3$  in the "plateau region" in  $0.5\text{M}$ -azide solutions is closer to the expected value and again falls off at high acetone concentrations.

The decrease in the nitrogen yield, below the "plateau region" value, suggests that the acetone interacts with the hydroxyl radicals. This is supported by the marked decrease of the nitrogen yield which occurs when the azide concentration is lowered at constant acetone concentration ( $5 \times 10^{-4}\text{M}$ ) (Fig. 6).

A possible mechanism is the abstraction of a hydrogen atom from the acetone; the influence of the acetone upon the nitrogen yield is so large as to make the rate of this reaction faster than that between methanol and the hydroxyl radical, a result in strong contrast to the results of Merz and Waters.<sup>3</sup>

As nearly all the nitrogen in the "plateau region" will come from the recombination of  $\text{N}_3$  radicals, the nitrous oxide yield would be expected to be quite high. The experimental figure for  $G(\text{N}_2\text{O}) = 0.17$  is to be compared with the nitrous oxide yield from  $0.1\text{M}$ -azide in the presence of  $0.1\text{M}$ -methanol where  $G(\text{N}_2) = 5.05$  but  $G(\text{N}_2\text{O}) = 0.03$ . In view of the results obtained in the radiolysis of the alcohol-azide solutions, the addition of methanol and propan-2-ol in the "plateau region" should result in a decrease of the nitrogen yield, this decrease being governed by the appropriate rate constant ratio (*e.g.*, for methanol by  $k_9/k_{18}$ ). Somewhat surprisingly, the nitrogen yields tend to a limiting value of *ca.*  $G(\text{N}_2) = 2.0$  for both methanol and propan-2-ol (Fig. 7).

*Azide Solutions in the Presence of Formaldehyde.*—Formaldehyde has been found to react with  $\text{H}_2\text{O}^-$ , so it seemed likely that the addition of formaldehyde to azide solutions would produce a similar pattern of results to those found with acetone. A sharp decrease in the nitrogen yield does occur, but the limiting value  $G(\text{N}_2) = 7.5$ , is far too high to correspond to removal of  $\text{H}_2\text{O}^-$  (Fig. 8). As the nitrogen yield decreases, that of hydrogen increases, and also reaches a limiting value which corresponds to a  $G(\text{H}) 0.3$ . The formaldehyde thus reacts very much faster with hydrogen atoms than does methanol, a result

<sup>3</sup> Merz and Waters, *J.*, 1949, S13.

in keeping with other experiments.<sup>4</sup> Therefore, it seems likely that the  $\text{NH}_2$  radicals also react rapidly with formaldehyde. The fall in the yield of nitrogen from  $G(\text{N}_2) = 10.2$  to 7.5 could be a result of the removal of  $\text{NH}_2$  radicals from reaction (21). If this explanation is correct, then no reaction between  $\text{H}_2\text{O}^-$  and formaldehyde has occurred, so this reaction must be very much less effective than that between acetone and  $\text{H}_2\text{O}^-$ .

#### EXPERIMENTAL

The experimental procedures were the same as those described in the preceding paper, apart from the following additions.

*Evacuation and Collection of Gaseous Products.*—The loss of acetone which occurred during evacuation of azide-acetone mixtures was found by estimation of the acetone content before and after evacuation. This loss depended on the acetone concentration and was *ca.* 5–15% for the concentration range  $8 \times 10^{-5}$ – $2 \times 10^{-3}$ M-acetone. The gaseous products were collected over solid carbon dioxide-acetone traps as it was found that nitrogen was retained to a small but significant extent by liquid air. To avoid too much contamination of the gaseous products these traps were cleaned after each collection.

*Gas Analysis.*—The presence of methanol, from 5 to 10 moles % in the gas samples, resulted in a slightly greater uncertainty in the nitrogen and nitrous oxide content, due to contributions to *m/e* 32 (air peak) and *m/e* 30 (reference peak for nitrous oxide) from the methanol. In the propan-2-ol experiments, samples were contaminated by acetone ( $\sim 3.0$ ), propan-2-ol ( $\sim 0.4$ ), propene ( $\sim 3.5$ ), and methane ( $\sim 1.5$  moles %). However, there was no serious interference with the determination of hydrogen, nitrogen, and nitrous oxide.

*Analysis of Solutions.—Ammonia.* In methanol-azide mixtures, ammonia was determined by the method described in Part I, unirradiated mixtures of methanol, azide, and standard ammonium chloride solution being used to establish the time at which the correct optical density was reached.

*Acetone.* Irradiated azide-propan-2-ol mixtures were analysed for acetone by the salicylaldehyde method.<sup>5</sup> The presence of sodium azide did not interfere with the determination.

*Ethylene glycol.* The glycol content of irradiated mixtures of azide and methanol was determined, after the removal of azide, by a modification<sup>1</sup> of Aspinall and Ferrier's method.<sup>6</sup> The azide was removed by acidification with sulphuric acid, followed by boiling. Experiments with standard glycol solutions showed that no loss of glycol was incurred by this procedure.

*Formaldehyde.* Formaldehyde was determined by a modification<sup>1</sup> of Johnson and Scholes's method.<sup>7</sup> The azide ion did not interfere.

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<sup>4</sup> Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., 1954, p. 594.

<sup>5</sup> Berntsson, *Analyt. Chem.*, 1956, **28**, 1337.

<sup>6</sup> Aspinall and Ferrier, *Chem. and Ind.*, 1957, 1216.

<sup>7</sup> Johnson and Scholes, *Analyst*, 1954, **79**, 217.