503. *Chemical Action of Ionising Radiations in Solution. Part XXII.* The Radiation Chemistry of Arsenite Solutions : the Action of X-Rays (200 kv) on Aqueous Solutions of Arsenite.*

By M. Daniels and J. Weiss.

The action of 200 kv *X*-rays on dilute aerated aqueous solutions of arsenite has been investigated over a wide range of pH. Arsenate is the only product in alkaline solution, but hydrogen peroxide is also formed in acid solution. A mechanism is proposed to account for the initial yields in acid solution, for the variation of initial yields with pH, and for the dependence of the yield on radiation dose.

Fricke and Hart [1] showed that *X*-irradiation of arsenite in the presence of oxygen afforded arsenate, and Schwarz, Losee, and Allen [2] determined the hydrogen yield (at one concentration and pH) in the absence of oxygen, using ^{60}Co γ-rays. The more extensive work of Haissinsky and Lefort [3] with α-particles and 50 kv *X*-rays appeared to produce a variety of unusual effects, in partial explanation of which reduction of arsenate by hydroxyl radicals was presumed.

This system allows wide variations of pH and it was decided to carry out a more detailed investigation using 200 kv *X*-rays.

Results

The major products of the irradiation were hydrogen peroxide and arsenate; the formation of these products, as a function of dose, in air-saturated 10^{-3}M-arsenite was investigated at pH 1·4, 8·2, and 12·7 with the results shown in Figs. 1, 2*a*, 2*b*, and 3.

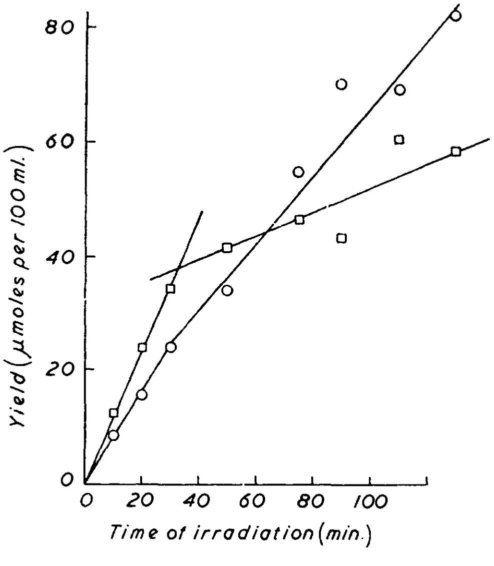

Fig. 1. *Irradiation of arsenite solutions* (10^{-3}M) *at* pH 1·4, *with* X-*rays* (200 kv). *Dose rate* = $3{\cdot}2 \times 10^{-7}$ mole ev ml.$^{-1}$ min.$^{-1}$.

Yield dose dependence for the formation of arsenate (○) *and hydrogen peroxide* (□).

At pH 1·4 the initial rate of formation of As$^{\text{V}}$ is linear with dose; the initial linear rate of formation of hydrogen peroxide clearly exceeds that of As$^{\text{V}}$, but a " break point," attributable to oxygen depletion, is found (Fig. 1).

At pH 8·0, whilst both rates of formation are initially linear, oxygen depletion leads to a pronounced consumption of peroxide and an increase in the rate of formation of As$^{\text{V}}$, until

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* Part XXI, *J.*, 1958, 2175.

[1] Fricke and Hart, *J. Chem. Phys.*, 1936, **3**, 596.

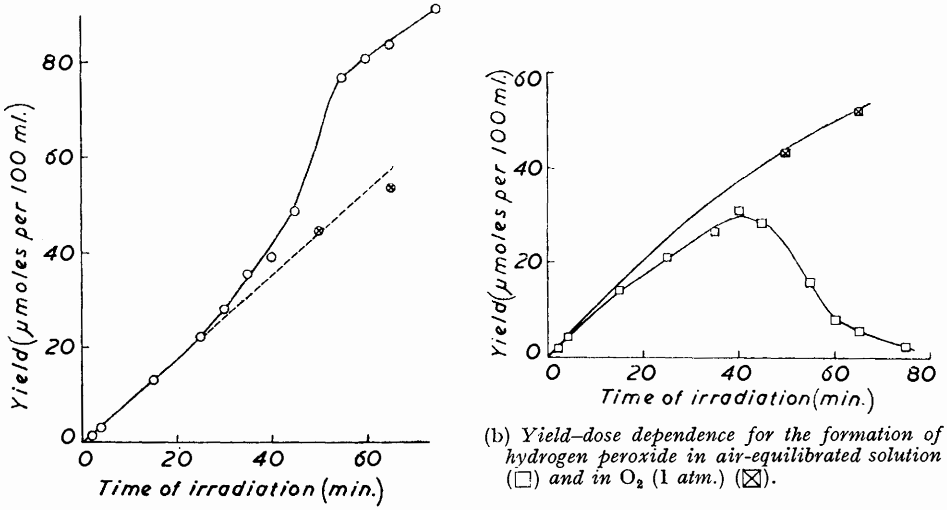
[2] Schwarz, Losee, and Allen, *J. Amer. Chem. Soc.*, 1954, **76**, 4693.

[3] Haissinsky and Lefort, *J. Chim. phys.*, 1951, **48**, 429.

all the peroxide has disappeared (Fig. 2*a* and *b*). In solutions saturated with oxygen (1 atm.) the behaviour is comparatively simple (Figs. 2*a* and *b*).

At pH 12·7, in aerated solutions, the rate of arsenate formation is initially linear and considerably greater than at lower pH; no hydrogen peroxide can be detected at this pH (Fig. 3).

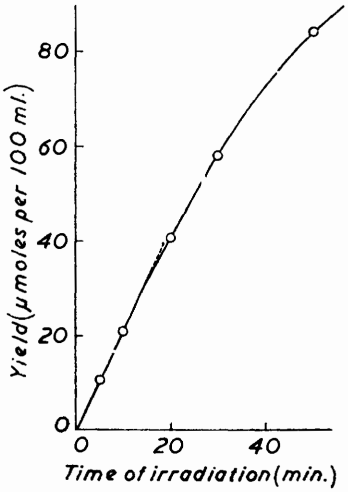
FIG. 2. *Irradiation of arsenite solutions* (10^{-3}M) *at* pH 8·0, *with* X-*rays* (200 kv). *Dose rate* = 3×10^{-7} mole ev ml.$^{-1}$ min.$^{-1}$.



(a) *Yield–dose dependence for the formation of arsenate in air-equilibrated solution* (○) *and in* O_2 (1 *atm.*) (⊗).

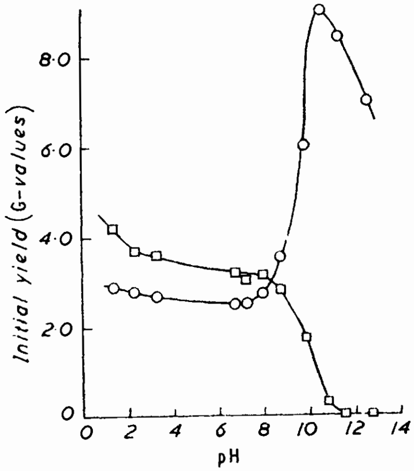
(b) *Yield–dose dependence for the formation of hydrogen peroxide in air-equilibrated solution* (□) *and in* O_2 (1 *atm.*) (☒).

FIG. 3. *Irradiation of arsenite solutions* (10^{-3}M) *at* pH 12·8 *with* X-*rays* (200 kv). *Dose rate* = 3×10^{7} mole ev ml.$^{-1}$ min.$^{-1}$.



Yield–dose dependence for the formation of arsenate (○).

FIG. 4. *Irradiation of arsenite solutions* (10^{-3}M) *with* X-*rays* (200 kv). *Dependence of the initial yields on* pH. *Dose rate* = 3×10^{-7} mole ev ml.$^{-1}$ min.$^{-1}$.



Arsenate (○). Hydrogen peroxide (□).

In view of the large variation in the yields of As^{V} and the initial absence of peroxide in alkaline solutions, the dependence of the initial rates of formation of peroxide and As^{V} on pH was investigated in greater detail, with the results shown in Fig. 4. Here the noticeable features are: in acid solution a continuous small decrease in the yields of peroxide and As^V with pH until neutrality is reached; and in alkaline solution a large increase in the yields of As^V and a decrease in those of peroxide, both effects reaching their maximum at pH 11; thereafter, peroxide as well as As^V contents decrease rapidly.

DISCUSSION

Arsenious acid and arsenic acid are here represented for simplicity as H_3AsO_3 and H_3AsO_4, often abbreviated as As^{III} and As^V respectively; complications such as complex formation (*e.g.*, meta-arsenites, etc.) and degree of hydration have little effect on the argument. The conversion, $As^{III} \longrightarrow As^V$, involves the consumption of two oxidising equivalents. If it occurs in stages by single-electron transfers, it is necessary to assume the existence of an unstable intermediate of quadrivalent arsenic having some structure such as $(HO)_3As^+$; this intermediate will be represented as As^{IV}. The ultimate step in the formation of arsenate may be a reaction such as the dismutation, $2As^{IV} \longrightarrow As^{III} + As^V$.

The radiation-chemical aspect will be discussed in terms of H, OH, H_2O_2, and H_2, as the " primary products," the yields per 100 ev being designated $G(H)$, $G(OH)$, $G_M(H_2O_2)$, and $G_M(H_2)$. The measured product yields will be designated as $G(As^V)$, $G(H_2O_2)$, etc.

Our results can then be reasonably accounted for, although the overall values of G(primary products) so derived appear, in general, to vary with the solute concentration.

(i) In the presence of dissolved oxygen the reaction:

$$H + O_2 \longrightarrow HO_2 \quad \ldots\ldots\ldots\ldots \quad (1)$$

does, under normal conditions, compete effectively for the hydrogen atoms. The situation presented in Fig. 1 then requires the following scheme of reactions to account for the high yields of peroxide and As^V:

$$OH + As^{III} \longrightarrow As^{IV} + OH^- \quad \ldots\ldots\ldots\ldots \quad (2)$$

$$HO_2 + As^{III} \longrightarrow As^{IV} + HO_2^- \quad \ldots\ldots\ldots\ldots \quad (3)$$

$$2As^{IV} \longrightarrow As^{III} + H_2O + As^V \quad \ldots\ldots\ldots \quad (4)$$

$$HO_2^- + H^+ \rightleftharpoons H_2O_2 \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

From this, $G(As^V) = \frac{1}{2}[G(OH) + G(H)]$, and $G(H_2O_2) = G(H) + G_M(H_2O_2)$, and the higher yield of peroxide is attributable to the contribution from the " molecular yield " and because, in general, $G(H) > G(OH)$. The importance of oxygen is shown by the " break point " (Fig. 1). Although there is some scatter in the yields after this point, the most important change is in the rate of formation of hydrogen peroxide, which decreases considerably, while for arsenate the change is quite small. After the " break point," hydrogen peroxide is still being formed, in amounts comparable to the molecular yield. It seems, therefore, that the reaction:

$$H + H_2O_2 \longrightarrow H_2O + OH \quad \ldots\ldots\ldots\ldots \quad (6)$$

cannot be taking place under these conditions. From the net rate of oxidation of arsenite after the " break point," it appears that not only OH but also H_2^+ act as oxidising species; the latter could react as follows:

$$As^{III} + H_2^+ \longrightarrow As^{IV} + H_2 \quad \ldots\ldots\ldots\ldots \quad (7)$$

(ii) At pH 8·0, there is initially the same behaviour as at the lower pH's, *i.e.*, eqns. (1)—(5) appear to be adequate, although at this pH, the equilibrium:

$$HO_2 \rightleftharpoons H^+ + O_2^- \quad \ldots\ldots\ldots\ldots \quad (8)$$

is practically completely shifted so as to give O_2^-, a reducing entity. However, it must be concluded that, as no marked decrease in the yields occurs, most of the radicals derived from hydrogen atoms still react according to equation (3). When oxygen consumption is complete, attack on the peroxide develops [presumably according to reaction (6)] with concurrent oxidation of the arsenite. Further, the peroxide consumed and the resulting "excess" of arsenate formed are roughly equivalent.

When the peroxide is completely consumed, the rate of formation of As^V decreases again, possibly owing to the back-reaction:

$$H + As^V \longrightarrow H^+ + As^{IV} \quad \ldots \quad (9)$$

(iii) At pH 12·7, no hydrogen peroxide is found at all and the rate of As^V formation is initially linear with dose, with only slight deviations at high conversions (Fig. 3). It is known that the reaction between hydrogen peroxide and arsenite is very rapid in alkaline solution;[4] this reaction is also quantitative and may contribute to the measured yield of arsenate.

The basic problem of the effect of pH is to determine whether it can be ascribed to ionisation of solutes or to some influence on the yields of the "primary products."[5] As regards the formation of As^V and hydrogen peroxide it may be considered in two parts.

(*a*) In the region pH 7—1 there is a steady increase in $G(As^V)$ from 2·5 to 2·85 and of $G(H_2O_2)$ from 3·2 to 4·2. The increase in $G(H_2O_2)$ is 0·95 which, according to the above discussion, should be a measure of the increase of $G(H)$ with decreasing pH; this is somewhat greater than values reported by Hart[6] and Gordon and Hart.[7]

On the basis of the simple mechanism proposed for the oxidation in acid solution, values of G(primary products) can be obtained, *viz.*: $G(H_2O_2) = G(H) + G_M(H_2O_2) = 4{\cdot}2$; $G(As^V) = \frac{1}{2}[G(H) + G(OH)] = 2{\cdot}9$. $G_M(H_2O_2)$ has been determined from experiments in the absence of oxygen to be 0·8, hence $G(H) \sim 3{\cdot}4$ and $G(OH) \sim 2{\cdot}4$. These values are somewhat lower than those found by Johnson and Weiss[8] who obtained $G(H) = 3{\cdot}5$ and $G(OH) = 2{\cdot}6$, derived from yields in the ferrous and the ceric system. The values given above lead to a net water decomposition of $G(-H_2O) = ca.\ 3{\cdot}8$.

(*b*) The pH range 8—13 shows further changes in the mechanism of oxidation. The rate of peroxide production decreases to zero while $G(As^V)$ increases rapidly. There are two salient features here: first, this behaviour occurs in the pH region in which arsenious acid ionises:

$$H_3AsO_3 \longrightarrow H^+ + H_2AsO_3^-;\ pK = 9{\cdot}22 \quad \ldots \quad (10)$$

secondly, the increase in oxidation of the arsenite is much more than equivalent to the peroxide disappearing. Hydrogen peroxide, if formed, reacts very rapidly with arsenite at this pH:

$$H_2AsO_3^- + H_2O_2 \longrightarrow H_3AsO_4 + OH^- \quad \ldots \quad (11)$$

However, the oxidation (11) can account only for half the arsenite formed. The rapid formation of As^V indicates a short chain-reaction and it is suggested that this is initiated by reaction of hydroxyl radicals with arsenite anions:

$$H_2AsO_3^- + OH \longrightarrow OH^- + H_2AsO_3 \quad \ldots \quad (12)$$

which gives the intermediate As^{IV}, reaction of which with oxygen could possibly give a chain reaction of the type:

$$R + O_2 \longrightarrow RO_2 \quad \ldots \quad (13)$$

$$RO_2 + RH \longrightarrow RO_2H + R \quad \ldots \quad (14)$$

$$RH + RO_2H \longrightarrow 2ROH \quad \ldots \quad (15)$$

where $RH = As(OH)_3$, $ROH = AsO(OH)_3$, $RO_2 = AsO(OH)_2O_2\cdot$, and $RO_2H = AsO(OH)_2O_2H$. This chain reaction could be terminated by reaction (4) or (16):

$$O_2^- + As^{IV} \longrightarrow O_2 + As^{III} \quad \ldots \quad (16)$$

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[4] Jamieson, *Amer. J. Sci.*, 1917, **44**, 150.

[5] Weiss, *Experientia*, 1956, **12**, 280.

[6] Hart, *J. Amer. Chem. Soc.*, 1955, **76**, 4198.

[7] Gordon and Hart, *ibid.*, 1955, **77**, 3981.

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

The rapid increase in $G(\text{As}^{\text{V}})$, attributed to a chain reaction, is halted at about pH 11. There the second ionisation of arsenious acid becomes significant, but as the ion HAsO_3^{2-} is even more reactive than H_2AsO_3^- (*e.g.*, autoxidation occurs above pH 12) this is unlikely to decrease $G(\text{As}^{\text{V}})$. The most feasible possibility is that ionisation of the hydroxyl radical:

$$\text{OH}^- + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{O}^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (17)$$

converts the oxidising hydroxyl radical into the reducing O^- ion, considerably decreasing the number of chain initiators. Hart, Gordon, and Hutchinson,[9] in work on radiation-induced ^{18}O exchange, give indications that effects due to such an ionisation can occur and estimate pK $\sim$9·0 for reaction (17). This would thus satisfactorily account for the behaviour observed.

EXPERIMENTAL

Materials.—Arsenite solutions (0·1N) were prepared by dissolving the weighed amount (2·473 g.) of arsenious oxide (" AnalaR ") in triply-distilled water (50 ml.) containing sodium hydroxide (" AnalaR "; 6 g.). The solution was diluted to 100 ml. and neutralised with 5 ml. of syrupy phosphoric acid as soon as possible, to avoid autoxidation (4). When the solution was to be analysed by the molybdate method (see below), neutralisation was carried out with sulphuric acid (" AnalaR "). 10^{-3}M-Solutions were prepared from this stock solution by dilution with triply-distilled water and the pH simultaneously adjusted by addition of dilute sulphuric acid or sodium hydroxide solution. In agreement with Reinders and Vles's reports [10] it was found that autoxidation of the neutralised stock solution was negligible during 3 weeks.

pH measurements were carried out with a glass-electrode system.

Radiation Procedure.—Irradiations were carried out with 200 kv X-rays at 15 milliamp. in an apparatus previously described,[11] on 100 ml. samples saturated with either air or oxygen. Dosimetry was carried out with ferrous sulphate in 0·8N-sulphuric acid, $G(\text{Fe}^{3+}) = 15{\cdot}6$ being used [11] and the dose rate being $3{\cdot}01 \times 10^{-7}$ mole ev ml.$^{-1}$ min.$^{-1}$.

Analysis.—Irradiation in acid solution produced hydrogen peroxide and arsenate; in alkaline solution only arsenate was found. These products were determined as follows. The hydrogen peroxide was determined colorimetrically by Eisenberg's pertitanic acid method.[12]

Arsenate was determined by two procedures: The first was a titrimetric method based on Gleu's work.[13] The initial arsenite concentration was determined by addition of the sample (5 ml.) to excess of ceric ammonium sulphate solution, 2 drops of osmic acid being used as catalyst. The excess of ceric salt was back-titrated against ferrous sulphate with *o*-phenanthroline as indicator. For the irradiated solution, the mixed solutions (ceric salt and irradiated solution) were set aside for 5 min., to permit the hydrogen peroxide to react. The osmic acid catalyst was then added and another 5 min. allowed before the excess of ceric ion was determined. By allowing for the previously determined hydrogen peroxide present in solution, the arsenate formed on irradiation could be obtained.

Being a titration procedure, the above could be used only for (relatively) large yields, and being a difference method it was liable to the accumulation of errors from the hydrogen peroxide determination. Accordingly, another method was developed, based on the formation of arseno(v)molybdate and its reduction to molybdenum-blue (see ref. 14). Hydrogen peroxide did not interfere. Agreement was found between the two methods, which are complementary; the molybdate method was used to determine initial rates of oxidation (*i.e.*, small conversions at low total dose), the ceric method for large doses which give inconveniently high optical densities in the molybdate method.

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[10] Reinders and Vles, *Rec. Trav. chim.*, 1952, **44**, 1, 30, 249.

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[12] Eisenberg, *Ind. Eng. Chem. Anal.*, 1943, **15**, 327.

[13] Gleu, *Z. analyt. Chem.*, 1933, **95**, 305.

[14] Daniels, *Analyst*, 1957, **82**, 133.