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Radiolysis of Aqueous Solution of Potassium Periodate

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Aqueous solutions of potassium periodate in neutral medium were irradiated with X-rays and with Cobalt-60 gamma rays. It was observed that the periodate on radiolysis is reduced only to iodate and no other reduction product was detected. A mechanism for the radiation induced reduction of periodate in aqueous solution is proposed and discussed. Effect of methanol on the course of radiolysis has also been studied.

Radiation induced reduction has been studied[1] in a number of cases of oxidizing agents. It is difficult, however, to make any definite correlation between such studies. Moreover, there are systems where the effect of radiation is little understood or has not been studied at all. Iodate and periodate, though well known as classical oxidizing agents, comprise such systems where not enough studies have been made to get a clear understanding of the mechanism of the radiation induced reduction. Radiolysis of iodate in acid or alkaline solution has been studied by earlier workers.[2–4] However, no study has yet appeared on the radiolysis of periodate. Radiation induced reduction of potassium periodate in aqueous solution in neutral medium forms the subject matter of the present investigation.

Experimental

Materials. Reagents such as potassium periodate, methanol, sodium bicarbonate, potassium iodide, *etc.* used in the investigation were all of analytical grade. Triply distilled water was used for preparing solutions for irradiation.

Irradiation. Irradiation with ^{60}Co γ-rays was carried out at 29°C at the Bhabha Atomic Research Centre, Trombay. The dose rate was determined with the Fricke dosimeter taking $G(\mathrm{Fe}^{3+})=15.5$ and measuring absorbances due to Fe^{3+} at 305 mμ. The dose rate was also determined by using ceric sulphate-sulphuric acid solutions. The Ce^{3+} yield was computed by measuring the depletion in absorbances due to Ce^{4+} at 315 mμ. The temperature dependence[5] of Ce^{3+} yield was taken into consideration and $\mathrm{G(Ce^{3+})}$ was accordingly taken as 2.34.

Exposures to X-rays were done at the Biophysics Division of the Institute by using unfiltered X-rays in a Mullard MG 150 tube operated at 80 KV and 9 mA. Average energy of the X-ray beam at the irradiation position as determined through aluminium absorption curves was found to be 27 keV. The dose rate was again measured with the help of the Fricke dosimeter. $G(\mathrm{Fe}^{3+})$ was, however, taken from Allen's mean curve[6] as 14.5 molecules per 100 eV. Deaeration of solutions was carried out by means of nitrogen gas containing less than 10 ppm of oxygen. The nitrogen gas, which was procured from Messrs. Indian Oxygen Limited, was washed with alkaline pyrogallol and then passed through the solutions for about half an hour.

Analytical Procedures. Periodate was determined[7] iodometrically in $\mathrm{NaHCO_3}$ solutions. When periodate is added to iodide solution which is 1 M in $\mathrm{NaHCO_3}$, the following reaction takes place:

$$\mathrm{IO_4^- + 2I^- + 2H^+ = IO_3^- + H_2O + I_2}$$

Iodate was also determined iodometrically by using the usual reaction in acid medium:

$$\mathrm{IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O}$$

Iodine liberated in both cases was extracted with benzene and the optical density of the benzene layer was measured spectrophotometrically at the absorption maxima, 297 mμ.

$\mathrm{H_2O_2}$ was determined with the help of titanium sulfate reagent.[8] All spectrophotometric measurements were carried out in a Hilger Uvispek photoelectric spectrophotometer.

Results and Discussion

Figure 1 shows the amount of decomposition of periodate as a function of absorbed dose due to γ- or X-irradiation. It is thus observed that the amount of decomposition is linear with dose up

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[1] A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions," D. Van Nostrand Co., Princeton, New Jersey (1961).

[2] G. L. Clark and W. S. Coe, *J. Chem. Phys.*, **5**, 97 (1937).

[3] N. R. Todd and S. L. Whitcher, *ibid.*, **20**, 1172 (1952).

[4] M. Haissinsky, J. Jove and W. Szymanski, *J. Chim. Phys.*, **61**, 572 (1964).

[5] C. J. Hochanadel and J. A. Ghormley, *Radiat. Res.*, **16**, 653 (1962).

[6] Ref. 1, p. 54.

[7] W. L. Lockhart and M. M. Jones, *J. Inorg. Nucl. Chem.*, **28**, 2619 (1966).

[8] G. M. Eisenberg, *Ind. Eng. Chem.*, **15**, 327 (1943).

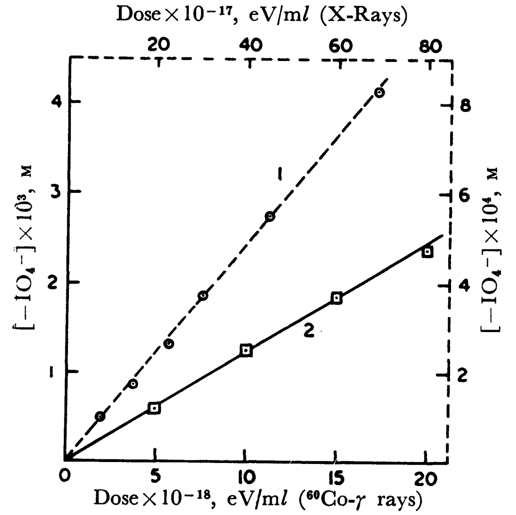

Fig. 1. Radiolysis of 5 mM KIO_4 solution in neutral medium with X-rays (1) and ^{60}Co γ-rays (2).

to an absorbed dose of about 10^{19} eV/m*l* and the radiolytic reduction yield, $G(-IO_4^-)$ was accordingly calculated from the slope. Both aerated and N_2-saturated solutions were irradiated and the decomposition yields in both cases were determined and $G(-IO_4^-)$ value was found to remain constant either in the presence or absence of dissolved oxygen.

It should be pointed out here that the radiolytic yield of the decomposition of periodate was ascertained by determining the concentration of periodate iodometrically both before and after radiolysis. In the iodometric procedure, as has already been mentioned, periodate is reduced only to iodate state, and if it is assumed that radiation induced degradation of periodate also leads to the formation of iodate only, then the molar concentration of iodate, as determined after reduction of periodate by iodide in $NaHCO_3$ medium and the removal of the liberated iodine from the system, should be equivalent to the molar concentration of periodate as taken initially before radiolysis. It is evident from Fig. 2, where the observed concentration of iodate is plotted as a function of absorbed dose, that the concentration of iodate is identical with that of initial periodate and that it remains fairly constant in the initial stages of radiolysis. When the absorbed dose, however, exceeds 60×10^{18} eV/m*l*, the observed iodate concentration is characterized by its linear decrease, which indicates that iodate is possibly undergoing radiolysis. It should also be pointed out that no periodate could be detected at such high doses, *i.e.*, all periodate ions that were present have been radiolysed. Moreover, the reduced states, such as I^- and I_2, which happen to be the characteristic products in the radiolysis of iodate, appear only at such high doses. But prior to such a limiting high dose no such reduction product could be detected. Therefore, the aforesaid linear decrease of iodate concentration with absorbed dose may in all probability be due to the radiolysis of iodate only, and if the dose corresponding to the point at which the straight line showing the linear decrease in observed iodate concentration meets on extrapolation the straight line showing its constant behavior, is taken as the point initiation of the process, then the iodate decomposition yield, $G(-IO_3^-)$, is found to have a value of 0.34 molecules per 100 eV which agrees well with our observed value in the case of radiolysis of iodate in neutral medium. However, this study on the radiolysis of iodate will, form the subject matter of a separate investigation. From what has been discussed above it can be concluded that periodate on radiolysis is reduced to iodate only.

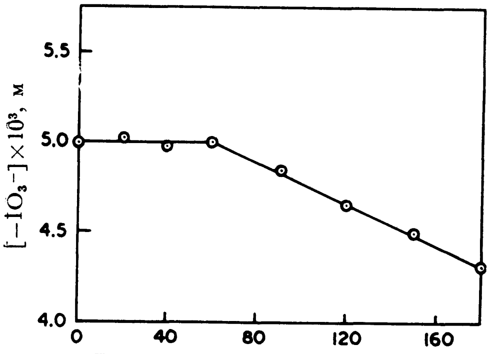

Fig. 2. Determination of iodate in the γ-radiolysed periodate solution after reduction of the periodate with KI in $NaHCO_3$ medium and removal of the liberated iodine through extraction with benzene. 5 mM KIO_4 solution was always initially taken before radiolysis.

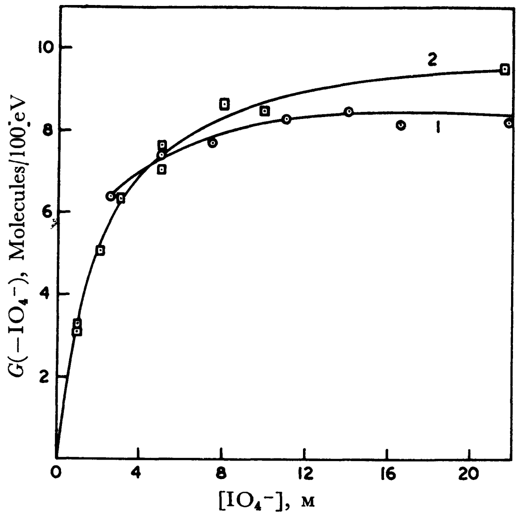

Fig. 3. Effect of initial concentration of periodate on $G(-IO_4^-)$. 1: irradiation with X-rays; 2: irradiation with ^{60}Co γ-rays.

Figure 3 shows the decomposition yield values as a function of solute concentration in cases where radiolysis is initiated by γ- or X-rays. It is evident from the figure that in the case of X-irradiation the decomposition yield, $G(-IO_4^-)$, initially increases but easily attains a steady value of 8.30 molecules per 100 eV. In the case of γ-radiolysis, however, the yields are strongly dependent on the initial concentration of periodate, and they have a tendency to attain a limiting value with increase of the solute concentration. It is therefore necessary to find the limiting G value where all the radicals generated in the solution are supposed to be swept away by the scavenger so that the stoichiometric explanation of the decomposition yields may be made easier. The limiting G value can be evaluated[9] by plotting reciprocals of G value against reciprocals of solute concentration and by extrapolating the straight line to zero reciprocal concentration. The results are shown in Fig. 4 and the limiting $G(-IO_4^-)$ value for γ-irradiation has thus been found to be 11.11 molecules per 100 eV.

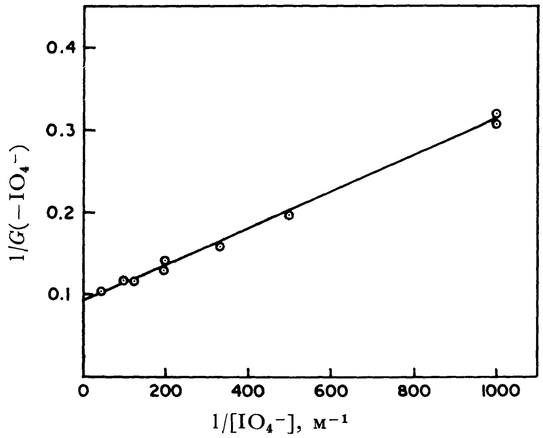

Fig. 4. Plot of the reciprocals of $G(-IO_4^-)$ against the reciprocals of $[IO_4^-]$ in case of γ-radiolysis.

It is well known [10] that water on absorption of γ-radiation gives rise to radical and molecular products as:

$$H_2O \rightsquigarrow H,\ OH,\ e_{aq}^-,\ H_2,\ H_2O_2 \qquad (1)$$

and the radiolysis of a dilute aqueous solution is initiated by an attack of the solute by these radical and molecular products.

It should be pointed out that no hydrogen peroxide could be detected in the solutions after irradiation. It can therefore be presumed that hydrogen peroxide takes part in some form of reaction during radiolysis. In fact, it is known[11] that hydrogen peroxide in neutral medium reacts with periodate. Although gaseous hydrogen was not determined in the solutions after irradiation, it is assumed that such a small amount of molecular hydrogen that is formed as a result of absorption of radiation by water, will not play any important role in affecting the course of radiolytic reduction taken under consideration.

Amongst the water radiolysis products, H or e_{aq}^- has a reducing action. If it takes part in one electron reduction process in the radiolysis of periodate, unstable IO_3 will be produced and this will immediately disproportionate itself into IO_3^- and IO_4^-. In that case the observed high reduction yield cannot be accounted for. Periodate is, however, known to be reduced to iodate very easily. If, on the other hand, it is assumed that H atom reduces IO_4^- to IO_3^-, then an equivalent amount of OH radicals will be produced in the system.

Now, as regards the mode of reaction of OH radicals in the system, one is naturally immediately inclined to treat them as oxidizing entities. But since a very high reduction yield has been observed in the system, one is tempted to think that OH radicals also take part in some sort of reduction processes. If the reduction of IO_4^- by OH comprises a two-electron process, as has been assumed for H atom reaction, then IO_3^- and an equivalent amount of HO_2 radical will be produced. It has already been stated that the reduction yield is not affected by the presence or absence of dissolved oxygen, which is clearly indicative of the fact that both H and HO_2 are equally effective in reducing periodate. If HO_2 is produced in the reaction of OH with IO_4^-, it will give rise to the development of a chain reaction. But a study of the dose rate dependence on the reduction yield does not, however, conform to such a view. Another possibility is that OH may reduce by an one-electron process. Then IO_3 and an equivalent amount of HO_2^- will be produced which in turn will reduce more periodate.

In the light of the observed results the following reaction sequences together with reaction (1) may be proposed for the radiolytic mechanism, e_{aq}^- for simplicity being represented by H:

$$IO_4^- + H \rightarrow IO_3^- + OH \qquad (2)$$

$$IO_4^- + H_2O_2 \rightarrow IO_3^- + H_2O + O_2 \qquad (3)$$

$$IO_4^- + OH \rightarrow IO_3 + HO_2^- \qquad (4)$$

$$2IO_3 + H_2O \rightarrow IO_3^- + IO_4^- + 2H^+ \qquad (5)$$

$$IO_4^- + HO_2^- \rightarrow IO_3^- + OH^- + O_2 \qquad (6)$$

From the proposed mechanism it follows that the reduction yield, $G(-IO_4^-)$, at the steady state will be expressed by the relation:

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[9] N. Matsuura, N. Shinohara and M. Takigawa, *Sci. Papers Coll. Gen. Educ., Univ. Tokyo,* **13**, 179 (1963).

[10] H. A. Schwarz, "Advances in Radiation Biology," Vol. 1, Academic Press, New York (1964), p. 1.

[11] I. M. Kolthoff and P. J. Elving, "Treatise on Analytical Chemistry," Part II, Vol. 7, Interscience Publishers, New York (1961), p. 375.

$$G(-IO_4^-) = \frac{5}{2}G_H + \frac{3}{2}G_{OH} + G_{H_2O_2}$$

Taking[12] $G_H=2.80$, $G_{OH}=2.22$ and $G_{H_2O_2}=0.71$ for γ-rays, the yield is calculated to be 11.04. Taking[13] again $G_H=2.09$, $G_{OH}=1.42$ and $G_{H_2O_2}=0.98$ for X-ray induced radiolysis in neutral solution, the decomposition yield, according to the above relation, comes out to be 8.33. The observed limiting yield values in cases of γ- and X-irradiation have, however, been found to be as 11.11 and 8.30 respectively. Thus it is evident that the observed decomposition yields are in good agreement with the values calculated in terms of the yields of the primary radical and molecular products.

If radiolysis of periodate is carried out in the presence of small amounts of methanol, the periodate decomposition yield is found to be significantly large. When methanol is present during radiolysis, the OH radicals will naturally compete for both CH_3OH and IO_4^- ions. By the reaction of OH with CH_3OH another reducing radical, CH_2OH, will be produced which in turn may reduce more periodate.

$$CH_3OH + OH \rightarrow CH_2OH + H_2O \qquad (7)$$

$$IO_4^- + CH_2OH \rightarrow IO_3^- + CH_2O + OH \qquad (8)$$

Any possibility that formaldehyde that is produced in reaction (8) may react with undecomposed periodate in neutral medium has been tested separately, but no such reaction within the concentration limits of the present investigation could be detected. Radiolysis of periodate in the presence of methanol will then comprise the reactions (1) through (8) and the reduction yield will accordingly be expressed by the relation:

$$G(-IO_4^-) = \frac{5}{2}G_H + \frac{3}{2}G_{OH} + G_{H_2O_2} + (G_H + G_{OH})\frac{K_7[CH_3OH]}{K_4[IO_4^-]}$$

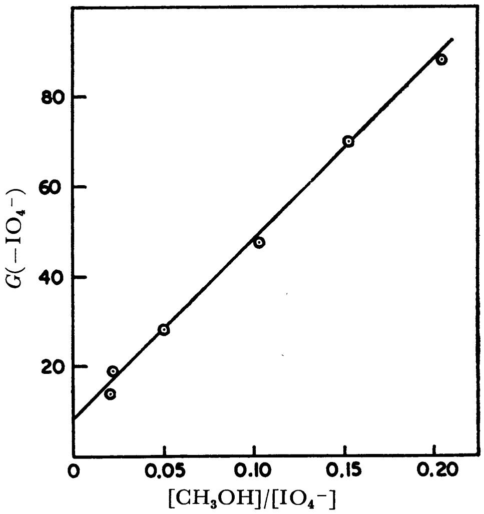

Fig. 5. Effect of methanol on X-ray induced radiolysis of potassium periodate in deaerated neutral solution.

A plot of $G(-IO_4^-)$ against $[CH_3OH]/[IO_4^-]$ will therefore yield a straight line. As has been stated previously, the intercept in case of the X-ray induced radiolysis will be equal to 8.33. Figure 5 shows the variation in the radiolytic decomposition yields with the ratios of the concentrations of methanol and periodate in the medium. A smooth straight line is thus obtained with an intercept of 8.3 which agrees well with the calculated value. This confirms the assumed kinetic behaviour in the proposed radiolytic mechanism. From the slope, the ratio of the rate constants K_7/K_4 is found to be 1.12×10^2.

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[12] J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley & Sons, New York (1964), p. 259.

[13] Ref. 1, p. 58.