Technical Papers

The Primary Radical Yield in Irradiated Water

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Intensive study of the reactions induced in various aqueous systems by ionizing radiation has led to estimates of the number of water molecules decomposed to form radicals by 100 ev of energy absorbed G_R. These estimates fall into two groups (*1*), a low group ($G_R \sim 3$–5) and a high group ($G_R \backsim 11$–13). The low values are derived from the formic acid-oxygen (*4*), the hydrogen-oxygen (*3*), and the ferrous ion (*4–6*) systems; the high values arise from the ceric ion (*2, 7*), dichromate ion (*8*), and hydrogen peroxide (*9*) systems. Other work in this laboratory has provided evidence in favor of a high value for G_R.

The existence of these two groups of values for G_R suggests that solutes may be divided into two classes possessing widely differing reactivity toward the free radicals H and OH. It is known, however, that the decomposition yields of the two solutes used by Hart —formic acid and ferrous ion—are constant over wide concentration regions. This has been taken to imply that they react with all the radicals formed.

It is here postulated that the absorption of ionizing radiation in water gives rise to two groups of radicals, one group being "available" only to the most reactive of solutes. The constant yield obtained with the ferrous system at varying concentrations is then ascribed to the reaction of the ferrous ion with all the radicals of the "universally available" group but with none of those of the second, less readily available group. It is postulated that most solutes, whatever their concentration, do not react with this second group of radicals, which disappear entirely by recombination, to form H_2O and perhaps H_2 and H_2O_2.

The G_R values of 3–5 for the low group and 11–13 for the high group suggest that the radicals of the first, universally available group are derived from ions (it is expected that 3 or 4 ion-pairs will be formed in water by the absorption of 100 ev of energy) while radicals of the second group are formed from excited water molecules. It would then be expected that the radicals of the second group would be less readily available for reaction with the solute, since an H atom and an OH radical are formed in close proximity and will rapidly recombine, unless the solute can react with one or the other, or both, before this occurs. It is significant that the high G_R values have been obtained with substrates of exceptional reactivity, such as hydrogen peroxide. Thus the ceric and dichromate ions are powerful oxidizing agents ($E = -1.61$ and -1.35 v, respectively).

These postulates may be used to explain some results obtained by Dale and his co-workers. It was shown (*10*) that the inactivation of the enzyme carboxypeptidase (C.P.) was independent of its concentration, except at very low concentrations, and this was interpreted as indicating that all the radicals reacted with the enzyme. Protection experiments then showed that, for example, thiourea was an excellent protector for C.P. (*11*), and this was thought to imply that thiourea also reacted extremely efficiently with the radicals formed by the irradiation of water. However, it was found that the liberation of sulfur from thiourea (*12*) followed a course similar to that for the deamination of glycine—this behavior having been previously interpreted as being due to the recombination of radicals. Thus, by two criterions (protection and the relatively high decomposition yield) thiourea is very radiosensitive, whereas by a third criterion (the shape of the yield versus the logarithm of the concentration curve) it reacts inefficiently with radicals.

Now it is reasonable to suppose that, in any division of solutes into two classes, the members of one class reacting almost completely and the members of the other reacting to a negligible extent with radicals formed from excited water molecules, there will be an intermediate class, the members of which will react more or less efficiently with such radicals, depending on the solute concentration. It is suggested that thiourea is a member of this class. It would then be expected, as was found, that the yield (molecules of solute destroyed or molecules of a particular product formed per 100 ev) would rise steadily with solute concentration as more and more of the radicals arising from excited water molecules react with thiourea, the latter reacting completely, even at low concentrations, with the radicals formed from ions. It would be predicted also that thiourea reacts more efficiently with radicals than, say, formic acid, and this is shown to be so by protection experiments (*11, 13*).

Three other reactions exhibit a steadily increasing yield with increasing solute concentration (*14*), namely, the radiolysis of trypsin and the deaminations of glycine and serine. The ammonia yields for the latter two reactions are 9 for a 20-percent glycine solution and 12.6 for a 5-percent serine solution. The somewhat different chemical natures of these two amino acids, together with the similarity of the yields obtained at the highest feasible concentrations, make it likely that chain reactions—the alternative explanation of the high yields, put forward by Dale (*15*)—do not occur. If this is so and if the reactions are brought about by H or by OH, but not by both, an ultimate G_R value of 9–13 is indicated. Clearly this is a lower limit, since the maximum yield may not be attainable because of the limited solubility of these compounds. However, it is significant that the yield for the serine deamination tends to become constant at the very

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highest feasible solute concentration (*16*), whereas for glycine the yield is still rising when the solubility limit is reached.

Stein and Weiss (*17*) found slightly lower yields for the deamination of glycine and, because of the unchanged yields in the presence of hydrogen or oxygen, considered that the radicals H, OH, and HO_2 were equally efficient in the deamination reaction. Such experiments are always open to the alternative interpretation that the substrate reacts so rapidly with the initially formed free radicals that the latter are not converted to other species by reaction with the added gas.

The fact that glycine is a poor protector for alloxazinadenine dinucleotide (*18*) suggests that these two solutes react with different entities arising from the irradiation of water. This lends support to the view that glycine reacts with H or OH but not with both.

A further phenomenon observed by Dale *et al.* (*13, 19*) in the study of protection phenomena is that of the "changing quotient." It was found that the efficiency of the protecting agent decreased as its concentration was increased. This was explained as being due to the inactivation of an enzyme (C.P.) molecule by a protector molecule previously "activated" by reaction with a radical. It is significant that all the substances for which the phenomenon was observed, namely, glucose, thiourea, sodium formate, dimethyl urea, and dimethyl thiourea, are known from protection experiments to react very efficiently with the radicals that deactivate C.P. (*13, 19*). If the concept of the formation of two groups of radicals in irradiated water is accepted, the explanation of the changing quotient must be modified to take into account the greater number of activated protector molecules present in the solution as the concentration of the protector is increased and it reacts with an ever-increasing proportion of the initially formed free radicals.

The validity or otherwise of the hypothesis here presented may be tested experimentally by measurements of the *G* values for the destruction of simple molecules over the greatest possible concentration range. Using radioactive isotopes, it is possible to make such experiments, measuring the disappearance of the substrate and not merely the appearance of a particular product.

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References and Notes

1. The *G* values quoted in this paper are based on a value of 20 for the yield of the ferrous ion dosimeter.
2. M. Haissinsky and M. Lefort, *J. chim. phys.* **48**, 368 (1951).
3. C. J. Hochanadel, *J. Phys. Chem.* **56**, 587 (1952).
4. E. J. Hart, *J. Am. Chem. Soc.* **73**, 1891 (1951) ; *J. Phys. Chem.* **56**, 594 (1952).
5. T. Rigg, G. Stein, and J. Weiss, *Proc. Roy. Soc.* (*London*) **211A**, 375 (1952).
6. C. B. Amphlett, *Discussions Faraday Soc.* **12**, 144 (1952).
7. M. Haissinsky, M. Lefort, and H. Le Bail, *J. chim. phys.* **48**, 208 (1951).
8. M. Lefort, P. Radhakrishna, and M. Haissinsky, *J. chim. phys.* **48,** 485 (1951).
9. F. S. Dainton and J. Rowbottom, *Trans. Faraday Soc.* **49**, 1160 (1953).
10. W. M. Dale, L. H. Gray, and W. J. Meredith. *Trans. Roy. Soc.* (*London*) **242**, 33 (1949).
11. W. M. Dale, *Brit. J. Radiol.* Supp. No. 1 (1947), p. 46.
12. W. M. Dale and J. V. Davies, *Nature* **163**, 64 (1949).
13. W. M. Dale, *Discussions Faraday Soc.* **12**, 293 (1952).
14. W. M. Dale, *J. chim. phys.* **48,** 245 (1951).
15. For example, W. M. Dale, J. V. Davies, and C. W. Gilbert, *Biochem. J.* (*London*) **45**, 93 (1949).
16. W. M. Dale and J. V. Davies, *Nature* **166**, 1121 (1950).
17. G. Stein and J. Weiss, *J. Chem. Soc.* 3256 (1949).
18. W. M. Dale, *Biochem. J.* (*London*) **36**, 80 (1942).
19. W. M. Dale, J. V. Davies, and W. J. Meredith, *Brit. J. Cancer* **3**, 31 (1949).

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Three-Dimensional Movies without Special Equipment

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There follows a method for putting a binocular feeling of depth into the viewing of an ordinary single-strip moving picture without the use of any complicated or special equipment. Some related observations on a relevant class of physiological phenomena are also included.

A well-known technique for obtaining two pictures of an object from slightly different directions is to rotate slightly the object between exposures (for example, tilt a microscope slide by placing a hair under one side); a stereo pair is thus obtained. This idea has been extended to moving pictures by placing the object on a rotating table (*1*) and taking movies as it rotates through two complete revolutions. This long film is cut in half, and the two resulting filmstrips are shifted in phase between corresponding views by a few frames before simultaneous projection through two projectors. For x-ray movies, the system has been modified (*2*) by a projector that simultaneously projects frames No. 1 and 3, then 2 and 4, and so forth, of a single movie of the rotating subject. (The images in both of the foregoing cases are channeled to the proper eye, for example, with polaroid.) There is another method based upon a physiological effect that allows a person, during ordinary single projection, to see a delayed or previous image in one eye while the other eye sees the present image; this can be used to see depth in any ordinary moving picture that contains sufficient motion.

The time delay between the viewing of a scene and the arrival of the impression in the brain depends on the brightness of the scene, the time being a decreasing function of brightness. Thus, if a person views a pendulum from a direction perpendicular to the plane of swing and places a neutral filter before one eye, the bob will appear to swing in an ellipse, since that eye is supplying an image of a previous position which fuses with the other image to give a resultant position in front of or behind the plane of swing. Such effects are often associated with the name Pulfrich (*3*). A monocular demonstration can be given in a darkened room, using a cigarette with a glowing tip (brighter