References and Notes

1. L. F. Hass and W. L. Byrne, *Abstr. Intern. Congr. Biochem., 4th Congr., Vienna, 1958,* No. 4-16, p. 39.
2. G. F. Cahill, Jr., J. Ashmore, A. E. Renold, A. B. Hastings, *Am. J. Med.* **26,** 264 (1959).
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4. Eq. 1 is the quotient of the steady-state rate equations in the presence and absence of inhibitor for the following mechanism:

$$E + \text{G-6-P} \rightleftharpoons E - \text{G-6-P} \rightleftharpoons E - P + \text{Glucose}$$
$$\downarrow H_2O$$
$$E + \text{Orthophosphate}$$

The inhibition of glucose-6-phosphatase by glucose is not one of the classical types, competitive, noncompetitive, or uncompetitive [P. W. Wilson, *Respiratory Enzymes,* H. A. Lardy, Ed. (Burgess, Minneapolis, 1949), pp. 16–56], and is best described by the above mechanism and its rate equation (Eq. 3).

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Mean Lifetime of Free Radical Chains Determined by a Flow Technique

Abstract. When radiolysis is induced in chloral hydrate solution flowing through a glass coil wound around a lead brick and irradiated from one side only, the rate of reaction depends on the flow rate. The effect resembles that for intermittent irradiation and makes it possible to estimate the mean lifetime of the free radical chain.

Intermittent irradiation techniques have been widely used in photochemistry (*1*) and to a lesser extent in radiation chemistry (*2*) for the determination of mean life-times of free radical chains. The usual method of securing intermittency is to employ a rotating sector between the source of radiation and the material being studied. Alternative methods include the reciprocating source method (*3*), in which the source is repeatedly removed from the reaction vessel and replaced in it after a short time interval, and the rotating source method, in which the cells containing the solution to be irradiated are mounted on a wheel which is rotated past an aperture in a shield containing a Co^{60} source (*4*). A somewhat different approach to the problem has been reported by Goldfinger and Heffelfinger (*5*). Radical formation was initiated in a mixture of styrene and benzoyperoxide by exposure to a mercury arc. After the stream of material had passed the illuminated region it fell freely, thus allowing chains to grow. Chains were terminated by means of a picric acid inhibitor, and by varying the distance between the source of radiation and the picric acid solution, the half-life of the styrene free radical chain could be determined.

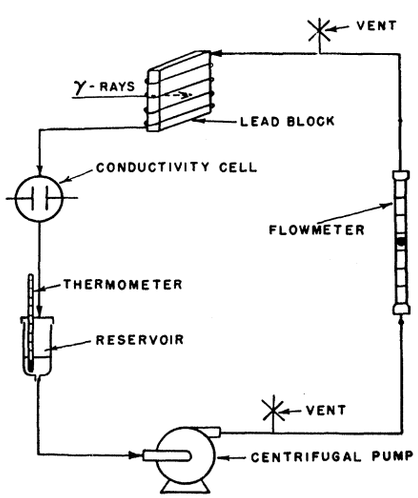

Fig. 1. Diagram of flow system; a 90-c Co^{60} source is housed in the lead cylinder.

Yet another method of achieving intermittent irradiation is to use a flow system in which the material flows past the Co^{60} source in such a way that it receives successive bursts of radiation. A brief description of the application of this method to chloral hydrate solutions follows. The mean lifetime of the free radical chains in 1*M* chloral hydrate solutions had previously been determined to be about 0.1 second by Freeman *et al.* (*6*), who used a rotating sector technique and gamma rays. The corresponding experiments for beta rays have also been reported (*7*).

Fisher U.S.P. chloral hydrate was used without further purification, and the amount of acid formed on irradiation was measured with a conductivity cell (*8*). For details see (*9*).

A 90-c Co^{60} source, housed in a concrete irradiation cave, was used as a source of gamma rays (*10*). The radiation dose was measured with the usual Fricke ferrous sulfate dosimeter and was found to be approximately 640 rad/min. The flow system is indicated diagrammatically in Fig. 1. The solution was pumped by means of a Cole-Parmer polyethylene 1/35 hp centrifugal pump through a flow meter, a reaction cell, a conductivity cell, and a reservoir. The reaction cell consisted of a glass coil of ten turns wrapped around a lead block in such a manner that a given volume element of solution would be subject to alternate "dark" and "light" periods. Flow rates were varied from 10 to 500 ml/min. The inside diameter of the tubing was 5.1 mm. The lengths of tubing exposed ("light" period) and unexposed ("dark" period) were 13.7 and 20.4 cm, respectively. Thus, for a flow rate of 500 ml/min, the "light" and "dark" periods were 0.34 and 0.52 seconds, respectively.

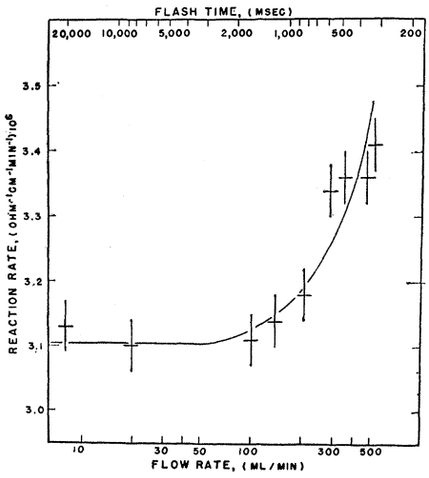

Fig. 2. Change in reaction rate versus flow rate.

Figure 2 shows the change in rate of reaction with rate of flow for 0.5*M* chloral hydrate solution at 25°C and at a *p*H of 4.60. The curve resembles that obtained by the rotating sector method (*6*) and indicates that the irradiation time in the region of reaction-rate increase is comparable to what would be expected if there were a strict parallel between intermittency in space and time. If we assume a complete parallel, the indicated mean lifetime of the chain is of the order of 1/5 second. Because of the dimensions of the reaction zone (4 by 4 in.) and its proximity to the Co^{60} source, the dose rate was not uniform, and thus a more detailed analysis of the experiment is not warranted. However, the results do serve to illustrate the possibilities of the method, which would appear to have wide applicability in both radiation chemistry and photochemistry.

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