was taken from the literature[4] and the ratio k_{16}/k_{14} was evaluated to be 0.16.

In the region oa the main competition is that of Fe(II) and Sn(II) for OH radicals. Fe(II) reacts with essentially all H_2O_2. Sn(II) reacts with nearly all H atoms as is indicated by the fact that the chief competitor, Fe(II), which produces H_2 on reaction with H, does not react appreciably with H until the Sn(II) is nearly depleted (region ab). The rate equations for region od and oa then become

$$G(Sn(IV)) = [G_{H_2O_2} + G_{OH}]$$
$$\left[\frac{(k_3/k_{13})(Sn(II))}{(k_3/k_{13})(Sn(II)) + (Fe(II))}\right] \quad (21)$$

$$G(Fe(II)) = G_H - G_{H_2O_2} + [G_{OH} + G_{H_2O_2}]$$
$$\left[\frac{(k_3/k_{13})(Sn(II)) - (Fe(II))}{(k_3/k_{13})(Sn(II)) + (Fe(II))}\right] \quad (22)$$

The integrated forms (equations 23 and 24) are shown as the solid curves od and oa. The ratio of rate constants k_3/k_{13} was evaluated to be 7.0.

dose = 120(Sn(IV)) −
$$93.2(Sn^0) \log [1 - (Sn(IV))/(Sn^0)] \quad (23)$$

dose = 65.8(Fe(II)) −
$$99(Sn^0) \log [1 - 0.585(Fe(II))/(Sn^v)] \quad (24)$$

For the system represented by the portion ab of the curve, a small concentration of Sn(II) is competing with Fe(II), Fe(III) and Sn(IV) for H atoms, and with Fe(II) for OH radicals. The only remaining adjustable factor is the reactivity of Sn(II) (relative to the other three solutes) for H atoms. The ratios of rate constants were ad-

justed until yields calculated using the general rate equations gave the best agreement with yields estimated from slopes taken from portion ab of the curve. On this basis the relative rate constants were $k_{14} : k_2 : k_{16} : k_{15} = 1 : \sim5000 : 0.16 : 0.081$. Because of the inaccuracy in estimating Sn(II) concentrations accurately at concentrations < 10 μM, and, in estimating slopes, ratios of rate constants involving k_2 are inaccurate. For example, an error of 50% in estimating the 10 μM Sn(II) concentration will make k_2/k_{14} in error by an order of magnitude. The ratios of rate constants not involving k_2 are believed to be accurate to ± 10%.

Radiolysis of Oxygen-free Solutions Containing Sn(II) and Fe(II) in 0.4 M H_2SO_4.—In degassed ferrous sulfate solution Fe(II) is oxidized with a yield $G(Fe(III)) = 8.2 = G_H + G_{OH} + 2G_{H_2O_2}$. Addition of Sn(II) lowers this yield until, at a concentration ratio (Sn (II))/(Fe(II)) > 0.02, oxidation of Fe(II) is completely suppressed. Sn(IV) and H_2 then are produced with a yield 0.45 = G_{H_2}. Typical experiments are shown in Fig. 4. The small amount of Fe(III) which may be present initially is first reduced to Fe(II). After the Sn(II) is nearly depleted, Fe(II) is oxidized at a rate which depends on relative concentrations of Sn(II), Fe(II), Fe(III) and Sn(IV). Inability to analyze accurately a small amount of Sn(II) in presence of a large amount of Fe(II) precluded the possibility of accurate kinetic analysis of the data from this particular system. However, the results confirm the fact that Sn(II) is reduced rapidly by H and oxidized by OH.

ON THE USE OF AQUEOUS SODIUM FORMATE
AS A CHEMICAL DOSIMETER

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On radiolysis, sodium formate in aqueous solution gives products which may be quantitatively titrated with acid permanganate. This system is proposed as a chemical dosimeter in the range 1–80 Mrad. and is particularly convenient for use in metal systems. The chemical change is proportional to the energy absorbed, and the yield of reductant ($G = 3.40$ mol. equiv./100 e.v.) is independent of dose rate, formate ion concentration over a wide range and temperature.

Introduction

Until quite recently the irradiation of liquids was largely carried out using glass vessels. With increasing use of fast electrons as a source of ionizing radiation, it has been found that glass is unsuitable in many applications. When electron beams are used, materials for irradiation cells are required (a) to be mechanically strong, (b) to be available in uniform and reproducible thickness, and (c) to conduct heat and electricity. Metals are obviously the most suitable materials of construction, and among those used, brass and aluminum have many advantageous characteristics.

Conventional dosimeters cannot be used in many metallic systems. Both the ferrous ion and ceric ion dosimeters have 0.8 N sulfuric acid as the sol-

vent medium. Air-free formic acid solutions are too acidic for use. The application of the continuous production of electrolytic gas from potassium iodide solutions[1] is limited mostly to rate measurements, and furthermore has the disadvantage of contaminating any metal system with traces of iodine. Oxalic acid solutions,[2] like those of formic acid, attack many metals.

A need exists, therefore, for a dosimeter which is suitable in commonly used metal systems.

Organic compounds immediately suggest themselves by virtue of their inertness to metals. However, we have been unable to find any common

(1) E. J. Hart and S. Gordon, *Nucleonics*, **12**, No. 4, 40 (1954).

(2) J. Sutton, I. Draganic and H. Hering, *Intl. Conf. Peaceful Uses of Atomic Energy*, **14**, 160 (1956).

organic liquid in which an easily measured chemical change occurs which is proportional to the energy absorbed over a wide range. In most systems the products are equally, if not more, reactive to intermediate ions and radicals than is the parent compound. Finally, there is the difficulty in obtaining the necessary purity for radiation work. Small quantities of impurities may be present, but they must be identified and shown not to affect the course of reaction.

The choice appears to be limited therefore to an aqueous system, using a neutral solute. We have found that the radiation-induced conversion of sodium formate to products quantitatively oxidized by acid permanganate is suitable for chemical dosimetry. The remainder of this paper will be devoted to testing the effect of the usual variables on the sodium formate dosimeter, and to measuring the absolute yield.

Experimental

Materials and Reagents.—All chemicals used were Merck Reagent Grade. The water used was either ordinary distilled water or water redistilled from alkaline permanganate. No difference in results was observed on interchanging the two sources of water.

Source of Radiation.—The source of radiation was an electron beam from a Van de Graaff accelerator of 3 Mev., 1 ma. capacity (High Voltage Engineering Corporation, Model KS). In our experiments the current was 20–40 μamp. and was used as a spot beam.

Absolute Measurement of Energy Absorption.—The experimental apparatus used in measuring the energy output of the electron beam is shown in Fig. 1. A wide-mouth (6'') dewar was filled with 1500 ml. of hydrogen-saturated water and centered with the lip one inch below the scanning tube of the accelerator. A collecting wire, dipped in the water, conducted the spent electrons to the accelerator controls. A film of polyethylene (7 mg./cm.²) was placed flatly over the dewar to prevent gross admission of air. The water was stirred by a small bar magnet actuated by a horseshoe magnet which rotated beneath the dewar.

The temperature of the water was measured by a Beckmann thermometer just before and after irradiation. On the average, a temperature increase of 3° was observed. The energy input into the water was taken as the heat capacity of the water and dewar multiplied by the measured temperature difference. The usual time–temperature extrapolations were made prior to and after irradiations, but in no case did the correction amount to more than 0.2%. The heat capacity of the dewar was measured by conventional mixing techniques and amounted to 160 ± 4 g. of water equivalent.

In order to compare the calorimetric measurements with the radiation-induced reaction in the sodium formate system, it was necessary to standardize the operation of the accelerator. The collected beam current was passed through a current integrator (Eldorado Electronics Company, Model CI-100) and the total charge accurately measured. Although the absolute accuracy of the voltage registered on the accelerator controls was probably no better than ±5%, preliminary tests showed that a reproducibility of ±1% was obtained at 2.5 Mev. This error was probably due to difficulty in setting the machine at exactly the same voltage on successive runs.

In a series of experiments, the total energy absorbed in the water was measured for irradiations at various voltages and total electron charges. This, in effect, monitored the output of the Van de Graaff accelerator for various voltage and current settings. In the data reported for sodium formate irradiations, the energy absorption was, in all cases, based on the calorimetric results.

Irradiation of Sodium Formate Solutions.—The volume of liquid used for energy calibration was inconveniently large for kinetic experiments. Accordingly, the dewar was replaced by an aluminum dish, 3.5 inches in diameter and 2 inches deep. During irradiations this dish was placed in a constant temperature bath and the contents stirred magnetically as before.
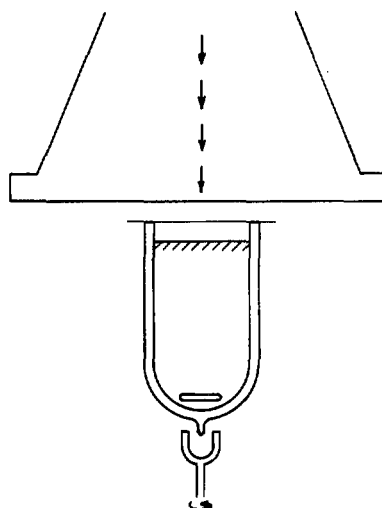

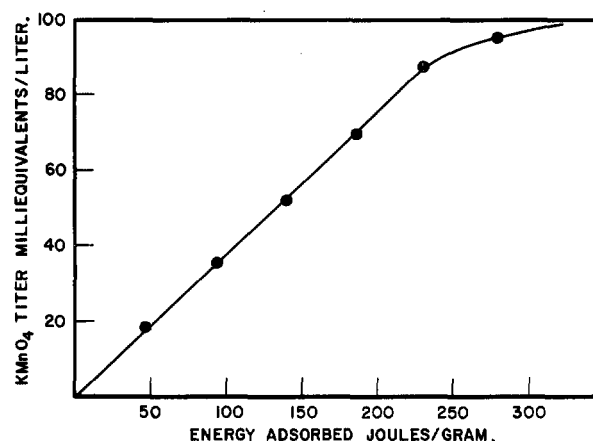Fig. 1.—Experimental arrangement for calorimetric measurement of the electron beam.

Fig. 2.—Equivalents of KMnO₄ titer as a function of energy absorbed for a 200-g. sample of 0.10 M sodium formate.

A 200-ml. volume of nitrogen-purged sodium formate solution was put in the dish, filling it to a depth of about 2 inches. Polyethylene film of the same thickness as before was placed over the dish and the unit centered beneath the electron beam at the same distance from the window as the dewar. Minor variations in positioning were shown to have no effect on the results. For a given voltage setting and total charge, it was assumed that the sodium formate solution absorbed the same amount of energy as the water in the dewar in calorimetric experiments. A few experiments using sodium formate solutions in the dewar confirmed this.

Analysis.—As will be shown in a subsequent paper, the products of irradiation are hydrogen gas and sodium oxalate, plus small amounts of formaldehyde and glyoxalic acid. Analysis was carried out by making the solution 2 N in sulfuric acid and titrating with 0.1 N potassium permanganate at a temperature above 80°. Under these conditions, a reproducible end-point is found. The total equivalent titer of permanganate is, for convenience, called the amount of reductant produced. The radiolysis products are stable, for aliquots of the irradiated solution gave identical values in determinations made immediately after irradiation and one week later.

Results

Effect of Energy Absorbed.—The production of reductant as a function of energy absorbed is shown in Fig. 2. The response is linear to at least 80% of complete reaction. Although some of the

products are known to react with H and OH radicals, they are well protected by formate ion under our conditions.

Effect of Sodium Formate Concentration.—Air-free solutions of sodium formate of various concentrations were irradiated to varying doses. All showed a response proportional to energy absorbed to at least 80% formate ion destruction. In Table I are found the yield of reducing equivalents for various initial formate ion concentrations. No effect of formate concentration on the reductant yield was found in the range 0.05–0.30 M. Above 0.5 M sodium formate, a slight increase in reductant yield was apparent. This may be due to direct action effects.

TABLE I

EFFECT OF SODIUM FORMATE CONCENTRATION
ON REDUCTANT YIELD

Initial concn. of sodium formate, moles/l.	Reductant yield Mol. equiv. per 100 e.v.
0.30	3.41
.10	3.40
.05	3.43

From these data it can be estimated that the useful range of this system is 1–80 Mrad.

Effect of Temperature.—Irradiations were made at various temperatures using 0.1 N sodium formate solution in a circulation loop system.[3] In the temperature range 0–40° no difference in reductant yield due to temperature was observed.

Effect of Oxygen.—When oxygen was bubbled continuously through the system during irradiation, erratic results were found. This was attributed to the hydrogen peroxide formed which may catalytically decompose and/or scavenge radicals. In most practical systems for which the dosimeter is to be used, the effect due to oxygen present in

(3) T. J. Hardwick, to be published.

solution from dissolved air is barely measurable. A simple purge with nitrogen or hydrogen removes all interferences.

Effect of Dose Rate.—The specific rate of energy absorption is difficult to estimate when a spot beam of electrons strikes a rapidly-stirred solution. However, with constant geometry and the same rate of stirring, an increase in the beam current by a factor of two did not change the yield of reductant.

pH Change.—The pH of sodium formate solutions in ordinary distilled water is about 7.5. On irradiation, the pH rises rapidly to 10–11 and remains steady. At this pH, aluminum is attacked slightly at temperatures above 35°. Traces of aluminum thus produced in the dosimeter solution do not affect the course of irradiation or the analysis. Disodium hydrogen phosphate in 0.1 molar concentration prevents any such attack on aluminum and does not change the reductant yield. Sodium bicarbonate is unsuitable as a buffer since, on making the initial sodium formate solution 0.1 M in sodium bicarbonate, an unexplained increase (20%) in the reductant yield was found.

Conclusion

The conversion of sodium formate in aqueous solution is suitable as a chemical dosimeter for light particle ionizing radiation. The useful range is approximately 1–80 megarad. The advantages of this system are: (1) linear response with energy absorption to at least 80% destruction; (2) in the range normally used, the effect of oxygen initially dissolved in the solution is almost negligible; (3) the response measured (*i.e.*, reductant production) increases from zero; (4) initial materials (sodium formate and distilled water) are readily available; (5) analysis follows a standard analytical procedure; (6) The system is non-corrosive to normal structural metals at room temperature; (7) the system is temperature independent.