MASTER

RADIATION CATALYZED CONVERSION OF
TRITIUM GAS TO TRITIATED WATER^a

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ABSTRACT

A survey of water production dependence on tritium concentration and external radiation fields has been made for the tritium-in-air concentration range of 0.01 to 1 Ci/m³. Results of reactions taking place under static conditions (in Pyrex flasks at 20°C) indicate that: (1) self-catalyzed rates may be first-order-dependent on tritium concentration, and (2) external radiation fields may cause a virtual steady-state condition to occur (in terms of additional self-catalyzed water production).

INTRODUCTION

The conversion of gaseous molecular tritium (T₂) to the water form (HTO) is accompanied by a potential increase in hazard to people. If the tritium is located where people actually come in contact with it, the conversion from T₂ to HTO represents a potential increase in hazard by a factor of 25,000. That is, the health risk from an inhalation exposure to HTO is 25,000 greater than that for the same airborne concentration of T₂.

Conversion kinetics of tritium have been studied for initial tritium concentrations between 16 and 330,000 Ci/m³ (Refs. 1-5). These concentrations are high compared to likely ambient conditions at fusion reactors in locations with potential human exposure. However, the lower part of the concentration range might occur following an unplanned tritium loss. Results of previous studies indicate that conversion of T₂ gas to HTO is first-order-concentration-dependent for initial T₂ concentrations between 10,000 and 330,000 Ci/m³ (Ref. 1), and second-order (or nearly second-order) for initial tritium concentrations between 16 and 4000 Ci/m³ (Ref. 2). Preliminary results at ORNL indicated that the conversion rate may revert to first-order for initial T₂ concentrations below 10 Ci/m³ in which case extrapolation of data from higher initial tritium concentrations would underestimate internal exposures to tritium.⁶

It is, therefore, not surprising that workers in fusion technology have been keenly interested in how fast T₂ converts to HTO, and which factors influence this rate. The data to be reported represent the first results from a program designed to determine some of these factors.

EXPERIMENTAL METHODS

The experimental protocol consists of making measurements of tritiated water (HTO) produced from gaseous tritium (T₂) under static conditions. Evacuated spherical flasks (about 350 ml) are cleaned and evacuated to ~10⁻⁴ Pa and are then backfilled with the desired amount of tritium gas (T₂). (The tritium gas is evolved by heating a uranium hydride bed.) To provide a reacting medium, the flasks are then backfilled to atmospheric pressure with a gas mixture whose composition depends on the type of experiment to be performed. In the experimental series under discussion, in which human safety is of concern and directly applicable data are desirable, air was chosen for the reactive gas. Other experiments which might be more directed at physical constant measurements would use mixtures of pure gases for the reacting medium.

Two types of experiments were performed in the present series. The first was the observation of self-induced production of tritiated water. After being filled, the flasks were sampled over time for reacted (HTO) and unreacted (T₂) tritium. In this manner a time series is established. The second type of experiment involved exposing a set of flasks to a source of radiation and then analyzing the flasks for reacted and unreacted tritium. A detailed discussion of the apparatus and sampling procedures has been presented elsewhere.⁷ In keeping with fusion safety studies needs, the reactant gas chosen was air, either dry (dew point - 70°C), moist (100% relative humidity, 20°C), or breathing (40% relative humidity, 20°C). Initial tritium concentrations were varied between approximately 0.01 and 1 Ci/m³.

Since radiation is one of the most likely reaction stimuli to be present at a fusion reactor, two different forms of radiation were used to expose reaction flasks: (1) a bare, unshielded reactor, and (2) a ⁶⁰Co source. The first source was chosen to provide conditions

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similar to those which might be found within a reactor hall during operation. Since the reactor used was unshielded, a relatively high percentage of neutrons were well above thermal energies. Further, the associated gamma field contained a broad mix of energies. A detailed description of the spectra from the reactor has been reported.² Of the reactor exposures, the reported doses are comprised of 88% neutrons and 12% gamma rays. The other radiation type used was ^{60}Co , to represent a pure gamma-ray field. Such a radiation field might be present at some locations and times at a fusion reactor.

RESULTS AND DISCUSSION

Self-Catalyzed Reactions

In the absence of external catalysts, a mixture of tritium gas, T_2 , and air will form water (HTO) much more rapidly than a mixture of protium, H_2 , and air. The reason for the difference is the self-radiation environment resulting from the decay of tritium atoms. The decay particles, with an average energy of 0.91 fJ interact with the atmospheric constituents to form reactive radicals, primarily H and OH. For mixtures including moisture, the primary reactive species include H_2O^+ , in addition to the radicals. These initiate a number of radical reactions leading to the formation of tritiated water.³

One of the more important questions being raised currently in fusion safety research is, "over what range of concentrations is the reaction to water first-order or second-order relative to concentration, or does the reaction have a different concentration dependence?" The self-initiated reaction was examined in this work for tritium concentrations between approximately 0.01 and 1 Ci/m^3 . Results of these studies are presented in Fig. 1. The data of Fig. 1 cannot unequivocally answer the question of whether the reactions are first or second order since: (1) the concentration range examined is rather small, and (2) the reactions were followed for only a few weeks. The data scatter over this time range masks any effects of small concentration changes due to the decay of tritium. However, several interesting observations can be made. First, within the first 24 to 48 hours (the crucial time for accidental tritium spills), the reaction seems to be well behaved and is less than 0.1% completed. No evidence was seen to suggest exceedingly rapid conversion to the water form. Second, from the beginning of each experiment, the reactions all proceed with calculated

Fig. 1. Self-catalyzed production of HTO as a function of time for mixtures of tritium in air. Calculated first-order reaction rates are 2.1 , 2.3 , 1.3 , and $2.7 \times 10^{-9} \text{ sec}^{-1}$ for the 0.63 -, 0.15 -, 0.11 -, and 0.01 - Ci/m^3 data, respectively.

first-order rates of approximately $2 \times 10^{-9} \text{ sec}^{-1}$. This value is two orders of magnitude higher than rates which might be anticipated by extrapolating the higher-concentration data of Casaletto et al.³ and of Belovodskii et al.⁴ The present data do not contain evidence of continuing the concentration-dependent trend evidenced in the data of Casaletto et al.³ and Belovodskii et al.⁴ In addition, for the present data which vary over about two orders of magnitude in tritium concentration, no significant concentration dependence is seen for the calculated first-order rate constants, which are all within a factor of two of one another. In fact, the first-order rate constant determined for the present data at $0.01 \text{ Ci}/\text{m}^3$ is within a factor of two from that calculated for the $100 \text{ Ci}/\text{m}^3$ data of Belovodskii et al.⁴ and Casaletto et al.³ Further, essentially no difference in rate constant is observed when comparing dry and breathing air. (Casaletto et al.³ also observed no difference when comparing rates using mixtures of tritium and dried breathing air or tritium and breathing air.) Thus, while not unequivocal, the data presented in Fig. 1 contains the first evidence of a low concentration regime for

reaction rate reversion from concentration dependence to concentration independence.

Radiation Catalyzed Reactions

Pure gamma field (^{60}Co). The presence of an external radiation field available to act as a reaction stimulus is virtually assured in many fusion-related situations where tritium may be found. A brief examination of the influence of high-energy photons on tritium reactions was made by Yang and Gevantman.⁹ They found that the yield in an isotopic exchange experiment was essentially monotonic with daily radiation exposures of 20,400 and 61,200 R at a rate of 40,800 R/hour with 250-KVP x rays. Their initial concentrations were 212 Ci/m³ with a water vapor density of 10 mg/l in an argon atmosphere. The data of Yang and Gevantman⁹ are in agreement with the results of Firestone¹⁰ and of Baxendale and Gilbert¹¹ who reported on radiation-induced water-vapor exchange. Yang and Gevantman⁹ interpret their data to indicate that the isotopic exchange reactions are first-order-dependent on the dose rate and proceed via radical intermediates. Further, for the range studied, external radiation exposures had no effect on the subsequent self- (tritium-decay) induced reaction. That is, upon cessation of exposure to x rays, additional HTO was formed at the rate anticipated.

The present data were taken in a concentration range two orders of magnitude lower than that cited above and for much lower concentrations of moisture. Data resulting from a ^{60}Co dose rate of 6400 rads/hour are presented in Fig. 2 for the concentration range 0.01 to 1 Ci/m³. In this figure, the dose plotted is only that from external irradiation and does not include the self dose which would be accrued after irradiation but prior to analysis. Rather different results are observed for the present data set than were reported by Yang and Gevantman.⁹ First-order rate dependence is only present for the first few hundred rads, above which the rate dependence appears to be concentration-dependent. For the highest concentration, the reaction to HTO proceeds with only a slight positive dependence on total dose, while for the lower concentrations, the reaction appears to go through a maximum and then attains an equilibrium at 0.2 to 0.5% of the tritium reacted. Thus it appears that radiation exposures may function very differently at different concentrations.

In addition to the depressed water formation, evidence is seen in Fig. 3 that the external irradiation may act as an inhibitor to

Fig. 2. Gamma-ray-induced production of HTO for mixtures of tritium in air. The gamma-ray dose rate was 6400 rads/hour.

Fig. 3. Comparison of HTO produced via self-catalyzed reactions versus gamma-ray-stimulated reactions for mixtures of tritium in air.

self-induced water formation. Experimentally, a set of flasks is filled to a predetermined tritium concentration and then backfilled to atmospheric pressure with air. For experiments involving radiation exposure, flasks are exposed to pre-determined doses shortly after filling and then (over a period of days or weeks) are analyzed for reacted and unreacted species. In this way, after exposure, there is additional time for self-catalyzed reactions to take place as reported by Yang and Gevantman.¹ In principle, the data could then be corrected by subtracting the quantity of HTO produced via the self-catalyzed reactions. The calculated values in Fig. 3 are taken from rate constants estimated from the data of Fig. 1 and the time between irradiation and analysis. Thus, points on the self-irradiation curves correspond in time (dose) sequence to points along the ^{60}Co plus self-irradiation curves. It is seen that self-catalyzed reactions proceed much more rapidly than do radiation-exposed samples. Data presented in Fig. 3 demonstrate quite convincingly that, for the concentrations examined in the present study, radiation exposure at a rate of approximately 10 times lower than that reported by Yang and Gevantman¹ results in virtually complete inhibition of self-catalyzed reactions subsequent to the external exposure.

Neutrons and gamma-rays. The final series of experiments was performed using a neutron plus gamma field, simulating conditions in a reactor hall during operation. In this series also, some unanticipated results can be noted (Fig. 4). The most striking is the loss of HTO with dose. Beyond about 5000 rads, the loss of water fraction appears to be linear with dose for the 0.2-Ci/m³ data sets, while the 0.01-Ci/m³ data set behaves similarly to the gamma-ray-exposed data at about that concentration (Fig. 2).

The dark symbols in Fig. 4 represent data points taken at 10,000 rads/hour and the open symbols were for 1500 rads/hour. For two of the three data sets, essentially no difference is seen between the 10,000- and 1,500-rad points, indicating a relative dose rate insensitivity for a given concentration or moisture level above 1500 rads/hour. Further examination of the early part of the two lower curves indicates a relative insensitivity to initial tritium concentration, similar to the ^{60}Co -exposed data.

Like the ^{60}Co -exposed samples, the neutron-exposed series also demonstrates that, for the concentration range 0.01 to 0.2 Ci/m³, exposure to radiation of the quality and rates

Fig. 4. Neutron- plus gamma-ray-induced production of HTO for mixtures of tritium in air. Note the moist air sample is saturated at 20°C. The (88%) neutron- plus (12%) gamma-ray dose rate was 1500 rads/hour for the open symbols and 10,000 rads/hour for the closed symbols.

herein described results in inhibition of later self-catalyzed reactions producing water.

CONCLUSIONS

The above data represent a survey of self-catalyzed and external-radiation-induced effects for tritium-in-air concentrations between 0.01 and 1 Ci/m³. The data presented represent departures from results anticipated by extrapolating from data taken by other researchers in the 10- to 1000-Ci/m³ range. Evidence has been presented which indicates that the often assumed second-order (concentration-dependent) rate for self-catalyzed reactions may not be present much below the 10-Ci/m³ range. An additional important observation is that between 0.01 and 1 Ci/m³, radiation may, for the doses and dose rates studied, result in a virtual radiation-induced steady state. That is, upon cessation of irradiation, no further additions of tritiated water occur by self-catalyzed reactions at 20°C when analyzed as long as two months

after irradiation. A similar observation of a radiation-induced steady state was made by Bardwell and Dyne¹² for radiation-induced exchange of deuterium between heavy water and dissolved hydrogen.

It is evident from the data presented that: (1) additional survey work is required, extending the present studies, and including other potential reaction stimuli, and (2) more detailed analytical work involving controlled gas mixtures should proceed so that reaction mechanisms can be better understood.

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