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Conversion of Tritium Gas to Tritiated Water

P. J. Papagiannakopoulos
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MASTER

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Health and Safety Research Division
Fusion Technology Studies

CONVERSION OF TRITIUM GAS TO TRITIATED WATER

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CONVERSION OF TRITIUM GAS TO TRITIATED WATER

P. J. Papagiannakopoulos and C. E. Easterly

ABSTRACT

The mechanisms of conversion of tritium gas to tritiated water (HTO) have been examined for several tritium gaseous mixtures. The physical and chemical processes involved in the self-radiolysis of such mixtures have been analyzed and the kinetics involved in the formation of HTO has been presented. It has been determined that the formation of the H and/or OH free radicals, as intermediate species, are of significance in the formation of HTO. Therefore, the problem of reducing the rate of formation of tritiated water in a mixture of gaseous tritium with atmospheric components is one of finding an effective scavenger for the H and/or OH free radicals.

1. INTRODUCTION

During the normal operation of a fusion reactor, small amounts of tritium will be lost to areas occupied by operational personnel and to the external environment. Gaseous tritium (HT) will interact with various atmospheric components and may form tritiated water vapor (HTO), which is substantially more hazardous to man than tritium gas. A knowledge of the formation rate of HTO is important in order to perform an analysis of health effects. Further, an understanding of the formation mechanism is necessary in order to develop appropriate methods to reduce the conversion rate of HT to HTO and, hence, to reduce the potential occupational risk within an enclosed area. Therefore, a study of the detailed mechanisms of the conversion of T_2 (HT) to HTO is appropriate.

Conversion of tritium to tritiated water has been explained in the past through oxidation and isotopic exchange mechanisms. Oxidation proceeds through the reaction

and the isotopic exchange mechanism proceeds through the reaction

The oxidation mechanism was introduced by Dorfman and Hemmer¹ in a study of the reaction between tritium and oxygen, initiated by the tritium beta radiation, at 25°C. The tritium pressure was in the range of 30-104 mm; the oxygen pressure was in the range of 69-218 mm, and there was a molar fraction of protium in the hydrogen reactant in the range of 0.055-0.831. The initial reaction rate $d[HTO]/dt$ was found to be proportional to the concentration of $[T_2]$, and was given¹ by the equation

$$\frac{d[HTO]}{dt} = k[T_2] (1 + bm_H) ,$$

where $k = 1.98 \times 10^{-6} \text{ sec}^{-1}$ is the rate constant of the reaction, $b = 0.3$ is the isotope effect correction, and m_H is the molar fraction of protium in the hydrogen reactant. Therefore, over the range of initial conditions, the reaction is of the first order and independent of the oxygen concentration.

The isotopic exchange mechanism was introduced by Yang and Gevantman² in a study of self-radiation of a mixture of tritium gas and water vapor, in an atmosphere of helium, at $22 \pm 2^\circ\text{C}$. The tritium pressure was in the range of 0.0159-0.2225 mm, the water vapor density was 5-17.5 mg liter⁻¹, and the helium pressure was in the range of 564-627 mm. The initial rate $d[HTO]/dt$ was described² by the equation

$$\frac{d[HTO]}{dt} = k[T_2]^2 ,$$

where $k = 4.17 \times 10^{-7}$ liter Ci⁻¹ sec⁻¹ is the rate constant of the reaction. Therefore, the reaction is taken to be second order and independent of water vapor concentration.

The above two mechanisms have also been employed by other workers³⁻⁵ for the explanation of their experimental results obtained under varying tritium concentrations and different gas mixtures. The tritium mixtures examined in the past and experimentally observed rates of HTO formation are presented in Table 1. From the literature examined, it is apparent that the mechanism(s) of conversion of tritium gas to tritiated water depend on (a) the composition of the gas mixture, (b) the concentration of each gas component, (c) the temperature, and (d) the presence of catalysts.⁶

In order to probe further the mechanism(s) of conversion of tritium gas to tritiated water, it is necessary first to examine the various physical and chemical processes that are involved in a gas mixture of tritium. These processes must be applied to different known gaseous mixtures to explain the experimental results. Once these physical and chemical processes are understood, appropriate methods for the elimination or reduction of the conversion of T₂ to HTO can be examined.

Table 1. The conversion of tritium to HTO in various gas mixtures

Mixture	T ₂ Concentration (Ci liter ⁻¹)	Conversion rate $\frac{d[\text{HTO}]}{dt}$ (Ci liter ⁻¹ sec ⁻¹)	Reference
T ₂ + H ₂ + O ₂	95-328	$1.98 \times 10^{-6} [\text{T}_2]$	<i>a</i>
T ₂ + O ₂ + Ar	0.09-90	$1.7 \times 10^{-8} [\text{T}_2]^{5/3}$	<i>b</i>
T ₂ + O ₂ + N ₂	0.018-1	$3.30 \times 10^{-7} [\text{T}_2]^2$	<i>c</i>
T ₂ + O ₂ + H ₂ O	<1	$1.20 \times 10^{-6} [\text{T}_2]^2$	<i>c</i>
T ₂ + Dry Air	0.015-0.8	$1.7 \times 10^{-7} [\text{T}_2]^2$	<i>c</i>
T ₂ + H ₂ O + He, N ₂ , Ar, Kr	0.05-0.7	$4.2 \times 10^{-7} [\text{T}_2]^2$	<i>d</i>
T ₂ + H ₂ O + Dry Air	6×10^{-4} -600	$1.7 \times 10^{-8} [\text{T}_2]^{5/3}$	<i>b</i>

^aL. M. Dorfman and B. A. Hemmer, *J. Chem. Phys.*, **22**, 1555 (1954).

^bL. F. Belovodskii, V. K. Gaevoi, V. I. Grishmanovskii, and N. V. Nefedov, *At. Energ.*, **38**, 379 (1975).

^cG. J. Casaletto, L. H. Gevantman, and J. B. Nash, "The Self-Radiation Oxidation of Tritium in Oxygen and Air," USNRDL-TR-565, Naval Radio, Def. Lab., San Francisco, Calif., 1962.

^dJ. Yang and L. H. Gevantman, *J. Phys. Chem.*, **68**, 3115 (1964).

2. RADIATION CHEMISTRY OF A TRITIUM GASEOUS MIXTURE

2.1 Physical and Chemical Processes

In a tritium gaseous mixture, the conversion of tritium gas to tritiated water occurs through a number of physical and chemical processes. The tritium molecules of the mixture decay by emitting beta particles (electrons) with an average energy of 5.7 keV, and a maximum energy of 18.6 keV.⁷ These beta particles have an initial kinetic energy much higher than the mean kinetic energy of molecules in the mixture. Therefore, they lose energy through collisions with the mixture molecules until they become thermalized and eventually disappear by recombination with positive ions or by attachment to neutral molecules. The molecules of the mixture absorb some of the beta-particle energy and undergo ionization or excitation, depending on the amount of energy transferred; this results in the formation of positive ions and excited molecules. The relative amounts of ionization and excitation depend on the energy of the primary electrons.⁸ A primary electron with an average energy of 5.7 keV when fully absorbed by the mixture produces approximately 170-190 ions, depending on the W-value⁹ (ionization efficiency) of the mixture.

The positive ions collide with neutral molecules and undergo charge transfer or ion-molecule reactions.¹⁰ A charge-transfer process preserves the chemical identity of the reactants, whereas an ion-molecule reaction does not. For a charge-transfer process to occur, the ionization potential of the neutral molecule must be lower than that of the positive ion. Neutralization of the positive ions through the processes of recombination with a thermal electron or a negative ion is not probable at atmospheric pressures and room temperatures. The fate of the excited molecules is mainly to decompose and form free radicals, and if the excitation energy is high enough, the free radicals may be in excited states.

The above processes result in the formation of free radicals which then induce a number of radical reactions. These radical reactions are responsible for the formation of the final products, in this case, the formation of tritiated water.

In the presence of high concentrations of water vapor, ion clusters¹¹ are produced by the interaction of positive ions and water molecules. The fate of the ions in the cluster is not known and is open to question.

2.2 Rate of Ion Formation

In a tritium gas mixture the rate of ion formation can be calculated from the tritium concentration and the fraction of the decay-product energy absorbed by the mixture.¹² The disintegration of n_{T_2} moles of T_2 results in the formation of $1.78 \times 10^{-9} n_{T_2}$ electrons sec^{-1} . The decay electron, with an average energy of 5.7×10^3 eV, forms $5.7 \times 10^3/W$ ion pairs. Therefore, the rate of decomposition of n_A moles of gas A to ion pairs will be

$$-\frac{dn_A}{dt} = 1.78 \times 10^{-9} \times (5.7 \times 10^3/W) n_{T_2} \times F f_A, \quad (2.1)$$

where F is the fraction of energy absorbed in the gas phase (not by the container walls in an experiment) and f_A is the fraction of F which is absorbed by gas A. For a gas mixture, $f_A = \mu_A v_A / \bar{\mu}$, where μ_A is the linear absorption coefficient of gas A for tritium beta particles, v_A is the mole fraction of gas A in the mixture, and $\bar{\mu}$ is the average linear absorption coefficient of the gas mixture given by $\bar{\mu} = \sum \mu_i v_i$. Calculation of the above quantities for various gas mixtures has been done by Mueller.¹³

The linear absorption coefficients of various gases for tritium beta particles at 25°C and 760 mm are presented in Table 2. Linear absorption coefficients at other temperatures and pressures can be found by multiplying the values given in Table 2 by the ratio of the density at the given conditions to the density at 25°C and 760 mm. Substituting the expression for f_A and dividing by n_A eq. (2.1) becomes

$$-\frac{dn_A}{n_A} = 1.78 \times 10^{-9} (5.7 \times 10^3/W) n_{T_2} \frac{F}{n_A} \frac{\mu_A v_A}{\bar{\mu}} dt, \quad (2.2)$$

or, using the ideal gas law,

$$-\frac{d[A]}{[A]} = 1.78 \times 10^{-9} (5.7 \times 10^3/W) \left(\frac{RT}{A} \right) \frac{[T_2]}{P_{\text{tot}}} F \frac{\mu_A}{\bar{\mu}} dt, \quad (2.3)$$

where P_{tot} is the total pressure, R is the ideal gas constant, T is the absolute temperature, and A is Avogadro's constant. At the initial stages of the reaction, the fraction $[T_2]/P_{\text{tot}}$ is essentially constant; therefore, at constant temperature the expression

$$k_A = 1.78 \times 10^{-9} (5.7 \times 10^3/W) \left(\frac{RT}{A} \right) \frac{[T_2]}{P_{\text{tot}}} F \frac{\mu_A}{\bar{\mu}}, \quad (2.4)$$

can be considered as constant.

Table 2. Absorption coefficients for tritium beta particles^a

Gas	Absorption coefficient $\mu(\text{cm}^{-1})$
H ₂	1.81
He	1.68
N ₂	11.0
O ₂	12.4
Ne	7.59
Ar	12.9
Kr	23.4
Xe	33.4
Air	11.3
H ₂ O	8.0

^aTaken from M. Mueller, Los Alamos Scientific Laboratory Report. LAMS-2580, October 10, 1961.

Hence, the equation

$$-\frac{d[A]}{dt} = k_A [A] \quad (2.5)$$

is obtained which gives the initial rate of decomposition of A molecules to ion pairs.

2.3. Dose Rate Calculation

For a tritium gaseous mixture in which the concentration of tritium is much smaller than the concentration of the other mixture components, the dose absorbed by the mixture will be approximately equal to the total energy liberated by the disintegrating nuclei. In a mixture with a tritium concentration of C millicuries per gram (equivalent to $3.7 \times 10^7 C$ dis/g·sec), the absorbed dose rate will be

$$\begin{aligned} \dot{D} &= 3.7 \times 10^7 C \left(\frac{\text{dis}}{\text{g} \cdot \text{sec}} \right) \times \bar{E} \left(\frac{\text{MeV}}{\text{dis}} \right) \times 1.602 \times 10^{-8} \left(\frac{\text{g} \cdot \text{rad}}{\text{MeV}} \right) = 0.593 \times C \times \bar{E} \text{ rad sec}^{-1} \\ &= 3.38 \times 10^{-3} \times C \text{ rad sec}^{-1}, \end{aligned}$$

where $\bar{E} = 5.7 \times 10^{-3} \text{ MeV}$ is the average energy released by tritium disintegration and transferred to the primary electrons.¹⁴ The total absorbed dose is given by the product of the above dose rate and the period of irradiation.

3. SELF-RADIATION OF VARIOUS TRITIUM MIXTURES

The rate of conversion of tritium to tritiated water has been evaluated in the past by performing experiments on mixtures with various compositions (Table 1). An understanding of the conversion mechanism of tritium gas to tritiated water can be reached by analyzing these experimental results in light of the radiation chemistry involved in a mixture of tritium with other gases.

3.1 Tritium, Oxygen, and Nitrogen Mixture

3.1.1 Physicochemical interactions

Experiments with mixtures of tritium, oxygen, and nitrogen were performed by Casaletto et al.³ In these experiments, the main component gas was nitrogen, and the total pressure of the mixture was 700 mm. Irradiation of such a mixture results in the formation of N_2^+ , O_2^+ , and T_2^+ positive ions and N_2^* , O_2^* , and T_2^* excited molecules. The ionic and excitation processes are

The N_2^+ ions are the main positive ions in the mixture and probably undergo the reactions:^{15,16}

The reaction (3.1) is predominant, especially for higher oxygen concentration. The O_2^+ ions undergo the reaction¹⁷

Reaction (3.2) results in the formation of N_2T^+ ions and tritium atoms. The tritium atoms induce a number of free radical reactions¹⁸ of which the most important are:

The above sequence is characterized by the presence of the radicals TO_2 , OT , and T , and water is produced via reactions (3.7) and (3.8). A small number of tritium atoms are removed through reaction

which is a much slower process than reaction (3.4). Removal of O_2^+ ions is accomplished by the three-body reaction (3.3) wherein they are converted to O_4^+ ions and O_2 molecules. The O_4^+ ions in the presence of water, form clusters through the following reactions:¹⁹

The N_2T^+ ions from reaction (3.2) in the presence of tritiated water undergo the reaction¹⁵

and at high T_2O concentrations clusters are formed through the reaction with an inert gas M

Higher hydrate formations up to $T_3O^+ \cdot (T_2O)_4$ have been observed in mass spectrometer experiments.²⁰ Removal of the T_3O^+ ions also takes place through the electron attachment process²¹

Thermalized electrons in the mixture are removed through the three-body electron attachment process²²

which results in the formation of O_2^- ions. The O_2^- ions are neutralized through the ion-ion reaction²²

Excited molecules H_2^* and O_2^* lose their excess energy through collisions and fall rapidly to a stable state. The processes of dissociative recombination and radiative attachment can be neglected since the electron density and the concentration of positive ions in these conditions are sufficiently low.

3.1.2 Kinetics for the formation of T_2O

The rate of T_2O formation can be given by the equation

$$\frac{d[T_2O]}{dt} = k_7[T][TO_2] + k_8[OT][T_2]. \quad (3.18)$$

It is assumed that the free radicals T , O , OT , and TO_2 are in steady state, and the following equations are obtained.

$$\frac{d[T]}{dt} = k_2[N_2^+][T_2] - k_4[T][O_2][N_2] - (k_5 + k_6 + k_7)[T][TO_2] + k_8[OT][T_2] = 0,$$

$$\frac{d[TO_2]}{dt} = k_4[T][O_2][N_2] - (k_5 + k_6 + k_7)[T][TO_2] + k_8[OT][T_2] - k_9[O][TO_2] = 0,$$

$$\frac{d[OT]}{dt} = k_6[T][TO_2] - k_8[OT][T_2] + k_9[TO_2][O] = 0,$$

$$\frac{d[O]}{dt} = k_7[T][TO_2] - k_9[O][TO_2] = 0.$$

Using the above equations, the rate of T_2O formation in Eq. (3.18) becomes

$$\frac{d[T_2O]}{dt} = \frac{k_2(k_6 + 2k_7)}{2k_5 + k_7} [N_2^+][T_2]. \quad (3.19)$$

Substituting the rate constant values¹⁸ results in

$$\frac{d[T_2O]}{dt} = 2.45 \times 10^{-9} [N_2^+][T_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}. \quad (3.20)$$

The form of this expression of water formation rate is in agreement with the experimental results of Casaletto et al.,³ in their experiments using mixtures of tritium, oxygen, and nitrogen,

$$\frac{d[N_2^+]}{dt} = 1.5 \times 10^9 \text{ ions cm}^{-3} \text{ sec}^{-1}, \quad [O_2] = 3.4 \times 10^{18} \text{ molecules cm}^{-3};$$

and $[T_2] = 2.7 \times 10^{15}$ molecules cm^{-3} . Since reactions (3.1) and (3.2) satisfy the relation

$$-\frac{d[N_2^+]}{dt} = \left\{ k_1[O_2] + k_2[T_2] \right\} [N_2^+] = \left\{ 5 \times 10^{-11} [O_2] + 2 \times 10^{-9} [T_2] \right\} [N_2^+] ,$$

it is found that

$$[N_2^+] \approx 6 \text{ ions cm}^{-3} .$$

Substituting the value of $[N_2^+] \approx 6$ molecules cm^{-3} in Eq. (3.20) results in

$$\frac{d[T_2O]}{dt} = 1.5 \times 10^{-8} [T_2] \text{ sec}^{-1} . \quad (3.21)$$

The above calculated value for the reaction rate constant $1.5 \times 10^{-8} \text{ sec}^{-1}$ is in good agreement with the experimentally found value $5.2 \times 10^{-8} \text{ sec}^{-1}$ for a mixture of tritium, oxygen, and nitrogen.³

3.2 Tritium, Oxygen, and Argon Mixture

Experiments with mixtures of tritium, oxygen, and argon were performed by Belovodskii et al.⁵ In these experiments the main component gas was argon, the total pressure of the mixture was 600–700 mm, and the oxygen concentration was 20% of the total. Irradiation of such a mixture results in the formation of Ar^+ , O_2^+ , and T_2^+ ions and Ar^* , O_2^* , and T_2^* , excited molecules. The ionic and excitation processes are

The Ar^+ ions are the main positive ions in the mixture and probably undergo the reactions:¹⁵

The reaction (3.22) is predominant, especially for higher oxygen concentrations. The T_2^+ ions can also induce the reaction¹⁵

but its contribution to the formation of T atoms is negligible in comparison with reaction (3.23). Removal of O_2^+ ions is through the reactions described in Sect. 3.1.1.

Reaction (3.23) results in the formation of ArT^+ ions and tritium atoms. In the presence of tritiated water, the ArT^+ ions undergo reactions similar to Eqs. 3.13 and 3.14.

The tritium atoms induce a number of radical reactions similar to those discussed in Sect. 3.1.1, and the production of T_2O can be given by the equation:

$$\frac{d[T_2O]}{dt} = \frac{k_2(k_6 + 2k_7)}{2k_5 + k_7} [Ar^+][T_2], \quad (3.25)$$

where k_2 is the rate constant of the reaction (3.23). Substituting the rate constant values¹⁸ results in

$$\frac{d[T_2O]}{dt} = 8.12 \times 10^{-10} [Ar^+][T_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}. \quad (3.26)$$

In these experiments, for a mixture with total pressure ~600 mm, the components are 400 mm argon, $[Ar] = 1.5 \times 10^{19}$ molecules cm^{-3} ; 120 mm oxygen, $[O_2] = 3.9 \times 10^{18}$ molecules cm^{-3} ; and 90 to 0.09 Ci liter⁻¹ tritium, $[T_2] = 9.2 \times 10^{17}$ to 9.2×10^{14} molecules cm^{-3} . The rate $d[Ar^+]/dt$ can be estimated for the various values of $[T_2]$, see Table 3. Since reactions (3.22) and (3.23) satisfy the relation

$$-\frac{d[Ar^+]}{dt} = \{k_1[O_2] + k_2[T_2]\} [Ar^+] = \{5 \times 10^{-11} [O_2] + 7 \times 10^{-10} [T_2]\} [Ar^+], \quad (3.27)$$

the values of $[Ar^+]$ can be found, and substitution in Eq. (3.26) results in the estimation of the calculated rate $d[T_2O]/dt$, see Table 3. These calculated reaction rate constants are in good agreement with the experimentally found rate constants.

Table 3. Calculated and experimental rates of HTO formation

$[T_2]$ Ci liter ⁻¹	$\frac{d[Ar^+]}{dt}$ ions cm^{-3} sec ⁻¹	$[Ar^+]$ ions cm^{-3}	$\frac{d[T_2O]}{dt}$ cal Ci liter ⁻¹ min ⁻¹	$\frac{d[T_2O]}{dt}$ ^a exp Ci liter ⁻¹ min ⁻¹
90	2.2×10^{11}	262	1.15×10^{-3}	1.8×10^{-3}
19.6	5.3×10^{10}	158	1.5×10^{-4}	1.41×10^{-4}
7.4	1.6×10^{10}	65	2.3×10^{-5}	2.8×10^{-5}
0.2	4.5×10^8	2.3	2.25×10^{-8}	7×10^{-8}
0.09	2.1×10^8	1.1	0.49×10^{-8}	2×10^{-8}

^aFrom data presented in L. F. Belovodskii, V. K. Gaevoi, V. I. Grishmanovskii and N. V. Nefedov, *At. Energ.*, **38**, 379 (1975).

3.3 Tritium, Water, and Helium Mixture

The mixture of tritium, water, and helium was examined experimentally by Yang and Gevantman.² In their experiments, the concentration of helium was much higher than that of water vapor. (The O_2 molecule concentration is taken to be 0.001% of the helium atom concentration; this amount of impurity is expected to be present in a research grade helium gas sample.) The rates of formation for He^+ ions was $\sim 10^9$ to 10^8 ions $cm^{-3} sec^{-1}$, for H_2O^+ ions $\sim 10^6$ to 10^5 ions $cm^{-3} sec^{-1}$, and for T_2^+ ions ~ 1 to 10^2 ions $cm^{-3} sec^{-1}$. Irradiation of the above mixture results in the following primary ionic and excitation processes.

The occurrence of H_2O^+ and OH^+ ions, formed by reacting thermal energy He^+ ions with H_2O , has been observed in mass spectroscopy experiments,²³ and their relative concentrations in ions cm^{-3} were found to be 17% and 83%, respectively. The positive ions produce the following ion-molecule reactions:^{15,24}

Reactions with T_2 , (3.31) and (3.33), are the least likely since the concentration of tritium is less than that of water. The main products of the above ion-molecule reactions are H_3O^+ ions and OH , H , and T free radicals. The H_3O^+ ions in the presence of water form clusters through the reaction with an inert gas M :

or through the electron attachment process

Higher hydrate formations occur up to $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_4$:²⁰

The OH, H or T, and O free radicals induce a number of free radical reactions,¹⁸ as follows:

From these reactions, water is formed in a number of ways. In order to determine the reaction or reactions that are predominant in the water formation, the relative concentrations of the free radicals should be known. An estimation of the order of magnitude of the free radicals concentration can be done in two steps. At first, the rate of formation of OH, H, or T, and O radicals is evaluated by assuming the steady state condition for the He^+ , H_2O^+ , and T_2^+ ions. Then by assuming the steady state condition for the H or T, OH, HO_2 , H_2O_2 , O, and O_3 radicals, it can be found that $[\text{H}] \sim 10^7$ to 10^8 molecules cm^{-3} , $[\text{OH}] \sim 10^6$ molecules cm^{-3} , $[\text{HO}_2] \sim 10^{10}$ molecules cm^{-3} , $[\text{H}_2\text{O}_2] \sim 10^{13}$ to 10^{14} molecules cm^{-3} , $[\text{O}] \sim 10^8$ to 10^{10} molecules cm^{-3} , $[\text{O}_2] \sim 10^{14}$ molecules cm^{-3} , and $[\text{O}_3] \sim 10^9$ to 10^{11} molecules cm^{-3} . Using these estimates the most predominant reactions are

From the above sequence of reactions, the rate of water formation is given by the relation

$$\frac{d[\text{H}_2\text{O}]}{dt} = k_{12}[\text{H}][\text{HO}_2] + k_{14}[\text{H}][\text{H}_2\text{O}_2] + k_{15}[\text{OH}][\text{H}_2\text{O}_2] + k_{16}[\text{OH}][\text{H}_2] + k_{17}[\text{OH}][\text{HO}_2]. \quad (3.49)$$

For the average mixture, $[\text{He}] = 2 \times 10^{19}$ molecules cm^{-3} , $[\text{H}_2\text{O}] = 4.1 \times 10^{17}$ molecules cm^{-3} , and $[\text{T}_2] = 1 \times 10^{15}$ molecules cm^{-3} , it can be found that $[\text{H}] \sim 10^7$ molecules cm^{-3} and $[\text{H}_2\text{O}_2] \sim 10^{13}$ molecules cm^{-3} . By substituting in Eq. (3.49), it is found that

$$\frac{d[\text{H}_2\text{O}]}{dt} = 2.36 \times 10^7 \text{ molecules cm}^{-3} \text{ sec}^{-1}, \quad (3.50)$$

which is approximately equal to the experimental value $d[\text{HTO}]/dt = 5.1 \times 10^7$ molecules $\text{cm}^{-3} \text{sec}^{-1}$, obtained by Yang and Gevantman.² It can also be shown that for all mixtures the theoretically determined rate of water formation, using Eq. (3.49), is the same order of magnitude as the experimental rate.² Therefore, Eq. (3.49) gives an approximate expression of the rate of water formation.

In an experiment where nitric oxide, a free radical scavenger, was introduced in the mixture,² a strong reduction was observed in the formation of tritiated water. Namely, for $[\text{NO}] = 1.58[\text{T}_2]$ the rate of water formation was 4% of the expected without NO. This was due to the strong scavenging effect of NO on H and OH radicals. The reactions¹⁸

are more predominant than reactions (3.39), (3.41) to (3.44) which result in the formation of water.

4. DISCUSSION AND CONCLUSIONS

4.1 Basic Mechanisms of HTO Formation

The conversion mechanisms of tritium to tritiated water have been examined for the three gaseous mixtures (T_2 , O_2 , N_2), (T_2 , O_2 , Ar), and (T_2 , H_2O , He).

For the tritium, oxygen, and inert gas mixtures, the mechanism of conversion starts with the formation of tritium atoms through the reaction

where M is an inert gas. The tritium atoms react with oxygen and inert gas molecules through the reaction

which then initiates a number of radical reactions, leading to the formation of water. It has been found that the calculated rate of water formation is about equal to the experimental rate.

For the tritium, water, and helium mixture, the primary ionic and excitation processes result in the formation of He^+ , H_2O^+ , and OH^+ ions, which induce the ion-molecule reactions:

The H_3O^+ ions form ion clusters and the OH, H or T, and O radicals initiate a number of radical reactions resulting in the formation of water. The 0.001% oxygen impurity in helium has been found sufficient to initiate adequate numbers of the important reaction

which then induce the rest of the radical reactions. A lower O_2 molecule concentration will reduce the occurrence of reaction (4.7) and therefore change the course of the subsequent radical reactions. Hence, in a tritium mixture, the relative O_2 molecules concentration is very important in the final formation of water which takes place through the following reactions:

From the above sequence of reactions, the importance of the OH, and H radicals in the formation of tritiated water, even in a moist gas mixture, becomes apparent. The introduction of a strong free radical scavenger, such as nitric oxide, results in the inhibition of the above reactions, and therefore the reduction of the tritiated water formation.

4.2 Prevention of HTO Formation

For tritium mixtures without water vapor, the formation of tritium atoms through ion-molecule reactions appears to be a very important process for the final formation of tritiated water. The tritium atoms initiate the radical reactions that result in the formation of HTO. Therefore, a method should be found either to prevent the formation of tritium atoms or to remove or to reduce them before they initiate the radical reactions. Then it would be possible to prevent or to reduce the formation of HTO.

In order to minimize the formation of tritium atoms, the ion-molecule reaction that produces the tritium atoms must be reduced. Therefore, a more efficient competing ion-molecule reaction should be encouraged by introducing into the mixture an appropriate additive gas. Further, the removal or reduction of the number of tritium atoms before they initiate radical reactions can be accomplished by introducing into the mixture a tritium-atom scavenger. Such a tritium-atom scavenger should remove all tritium atoms and result in a tritium-labeled compound less hazardous than HTO. The gases C_2H_4 and C_3H_6 have been used as scavengers of hydrogen atoms in the gamma radiolysis of ethane, propane, n-butane and n-pentane.²⁵ Thus, hydrocarbons could be used as effective scavengers of hydrogen atoms. A number of possible reactions between hydrogen atoms and hydrocarbons, together with their rate constants,¹⁸ are listed:

Ammonia, hydrogen sulfide, and formic acid can also be considered as possible hydrogen-atom scavengers. They operate by the reactions:

For tritium mixtures in the presence of water vapor, the formation of T and OH radicals appears to be a very important process for the final formation of tritiated water. Therefore, an additive gas should be found that will remove both T and OH radicals before they react with other radicals. There are a number of such T and OH radical scavengers which could be used. The problem is to choose the one that is less hazardous or forms products that are less hazardous than the HTO.

Hence, the problem of eliminating or reducing the conversion of tritium to tritiated water is reduced to one of finding an approximate OH and/or H scavenger for the given tritium mixture.

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