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Radiochemical Reactions between Tritium and Humid Air*

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Abstract — Radiochemical reactions between pure tritium (T_2) and moist air have been examined using real-time Raman spectroscopy. The reacting constituents were contained in a 1 cm³ quartz cell sealed by a quartz-to-metal seal leading to a valve. A near-stoichiometric mixture of T_2 and O_2 was introduced into the cell, and the time evolution of the composition was monitored at 297 K for twenty-nine days. The production of T_2O was observed in these experiments, for the first time unambiguously detected in Raman spectroscopy. T_2O exhibits a relatively weak vibrational band at ~ 2313 cm⁻¹. The radiochemical production of tritiated water did not occur in the expected 2:1 ratio, but rather with the O_2 disappearing totally when the T_2 was only slightly over halfway depleted. After the disappearance of O_2 , the T_2 partial pressure continued to decrease, but at a slower rate. The initial water in the moist-air mixture disappeared totally after about 15 hours, with no concomitant production of HT. A small quantity of CO_2 was also detected, presumably produced by radiochemically driven reactions with stainless steel components.

I. INTRODUCTION

Radiochemical reactions of elemental tritium (T_2) with various molecular species are of considerable importance to fusion reactor operations both from a safety perspective, in predicting potential consequences of accidental releases of tritium, and from a processing perspective, to characterize potential side reactions within nuclear-fusion fuel cleanup systems. Raman spectroscopy constitutes an attractive, non-invasive technique for *in situ* monitoring of tritium reactions with other species likely to be encountered in fusion plant operations [1-6]. Our earlier studies of tritium radiochemical reactions using real-time Raman spectrometry to observe the evolution of sealed mixtures in clean cells (for example, in the exchange between D_2 and T_2 to produce DT) [3] have yielded substantially different results from alternative approaches such as mass spectrometry in stainless-steel vessels [4]. Our earlier studies of mixtures of CO and tritium have shown a complex radiochemical reaction chain (including the transient observation of a polymeric-like "snow") leading to final products of CO_2 and T_2O [5]. Those experiments constitute the first Raman observation of T_2O reported in the literature; they are confirmed by the unambiguous Raman observations of T_2O in the experiments reported here.

This paper describes experiments aimed at elucidating the radiochemical reactions between tritium and humid air, conducted at TSTA over five weeks in February-March 1997. Tritium and humidified air were placed in a 1 cm³ cell, and

the composition was monitored using real-time Raman spectroscopy for twenty-nine days. Interestingly, we observed that the T_2 and O_2 concentrations did not diminish in the expected 2:1 ratio required for the production of tritiated water, but rather the O_2 concentration dropped significantly more quickly, with the T_2 concentration continued to diminish after all of the O_2 had reacted. These results suggest that tritium oxidation is not the sole mechanism of tritium depletion.

II. EXPERIMENTAL

A. Apparatus

A schematic of the experimental apparatus is shown in Fig. 1. The apparatus is located at the Tritium Systems Test Assembly (TSTA) in a glovebox to which has been added an extension ("gondola") to permit optical access for Raman spectroscopy. The gondola is rigidly attached to an optical table under the glovebox that supports the laser Raman apparatus and attached to the glovebox with a neoprene gasket. The quartz optical cell is attached to the gondola through an X-Y-Z displacement stage, and to the 316 stainless-steel gas manifold via a quartz-to-metal seal and an all metal stainless-steel valve (Nupro SS-BNV series). A stainless steel high vacuum system, constructed of conventional components made of 304 and 316 SS alloys, was employed to permit the mixing, addition, and removal of gases to the cell.

Fig. 1. Raman apparatus for studying radiochemical reactions.

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An Ar-ion laser (Spectra-Physics model 2040E-20), operating at 488 nm and 3 W, is used as the light source. Scattered light is collected at an angle of 90° relative to the incident beam and imaged by a camera lens into a 0.32 m spectrometer (Instruments SA, model HR320). Simultaneous measurements of all chemical species is accomplished using a multichannel Raman detector (intensified photodiode array, IPDA, Tracor Northern model TN6122A) at the output of the spectrometer. The spectrometer was outfitted with a 600 line/mm diffraction grating (Instruments SA) in order to observe all molecular species by vibrational Raman spectroscopy. Additional details are given in [3], [5], and [6].

B. Experiment

To initiate the experiment, purified tritium from a heated ZrCo storage bed, (in which the only impurities were HT and DT, each at the couple per-cent level), was loaded into the Raman cell at 201.6 torr, after which a reference spectrum was obtained. The cell was then isolated by a valve attached to the metal-to-quartz graded seal, and the excess tritium returned to the cooled ZrCo storage bed. The air to be mixed was extracted from a heated humidifier vessel and admitted into the manifold adjacent to the cell at a measured overpressure. The mixing was accomplished by opening the valve between the Raman cell and the manifold for about a second, while observing renewed stabilization of the MKS Baratron pressure gauge attached to the manifold, and then closing the valve. Raman signals for T₂ returned to the levels observed prior to mixing after a mixing transient of about 10 minutes, indicating that negligible tritium was lost during the mixing procedure.

Raman spectral acquisitions were initiated using integration intervals of 2 or 5 minutes during the first several hours and subsequent intervals of 15 minutes or longer. Spectra were acquired using the ISIS software provided by the IPDA manufacturer (Instruments SA). During the first 140 hours of the experiment, the Raman alignment was found to be sub-optimal; a subsequent realignment increased the signal-to-noise ratio by a factor of three. As this realignment slightly changed the relative ratios of Raman peaks from different species, small correction factors were applied to subsequent Raman ratios to provide essentially seamless trends. Throughout the course of the experiment the temperature varied between 22.6°–25.2°C.

Following the Raman acquisitions, the final pressure was determined by expanding the mixture into a known volume and reading the pressure using an MKS Baratron gauge. The final composition of the mixture was then assayed with a high resolution mass spectrometer (PATCO model 6-90-GQN).

C. Data Reduction

In analyzing the spectra, the area of the strongest Raman vibrational line was used. Interferences were occasionally encountered, such as the 546-nm room-light emission line (Hg) which lies close to the T₂O vibrational signal. Accordingly, only the T₂O signals recorded at night, while

TSTA room lights were off, were analyzed. Neither the Raman spectra nor the mass spectra displayed any traces of ammonias (tritiated or otherwise), implying a constant N₂ partial pressure throughout the experiment. As a result, the inevitable drifts in absolute Raman intensities, such as those due to diurnal temperature variations in the TSTA room, are conveniently removed by dividing the Raman signals from all other species by the N₂ Raman signal. From these ratios and assuming no mysterious disappearance of gas (such as leaks, which would have been detected by the glovebox tritium monitor), absolute partial pressures of T₂ and O₂ were derived from the following formula

$$P_i(t) = P_i(0) \frac{I_i(t) / I_{N_2}(t)}{I_i(0) / I_{N_2}(0)}, \quad (1)$$

where $P_i(t)$ denotes the partial pressure and $I_i(t)$ the Raman intensity of species i at time t . For constituents such as CO₂ and T₂O, for which no adequate Raman calibration exists, only approximate partial pressures could be estimated.

III. RESULTS and DISCUSSION

A. Raman Analysis

The composition of the initial gas mixture is shown in Table I. The H₂O partial pressure was estimated from early Raman spectra, with the caveat of substantial uncertainty (perhaps as high as a factor of 2) due to lack of calibration. Despite efforts to achieve high humidity, this H₂O partial pressure was certainly well below the dew point pressure of about 23 torr, indicating the need to develop more reliable humidification procedures in future experiments.

Table I
Initial and Final Partial Pressures

Species	Initial (torr)	Final (torr)
T ₂	201.6	14.7
O ₂	99.5	0.0
N ₂	370.9	371.6
T ₂ O	—	11
H ₂ O	4.6	0.0
³ He	—	2.0
Other (Ar, etc.)	4.6	4.6

The most significant radiochemical reaction expected in a mixture of tritium and air is the oxidation of tritium to form tritiated water,

Fig. 2 shows three representative Raman spectra taken during the experiment. (For clarity, two of the spectra are shifted along the ordinate.) The spectra show a steady depletion of O₂ and T₂ and a concomitant growth of T₂O, at a wavenumber of approximately 2313 cm⁻¹. (The peak at 2180 cm⁻¹ is from stray room light, as discussed Sect. II.C). The tritiated water peak is relatively weak, as one might expect from the behavior of normal (protiated) H₂O [7].

Fig. 2. Representative Raman spectra. The T_2 and O_2 are gradually depleted while T_2O is produced. (The peak at 2180 cm^{-1} is a Hg emission line from stray room light).

The time evolution of the molecular constituents is shown as ratios of peak areas to that of N_2 in Fig. 3 and as absolute partial pressures in Figure 4. Fig. 4 was constructed by substituting the data contained in Fig. 3 and Table I into Eq. 1.

It is apparent from a comparison of Table I and Figs. 2-4 that tritium and oxygen are not reacting in the 2:1 stoichiometric proportion expected from Eq. (2). In particular the O_2 disappearance occurred about 200 hours, at which time the T_2 was just slightly over half (62%) depleted. There appears to be an abrupt change in the T_2 slope coincident with the O_2 depletion. The production of T_2O commenced early and climbed monotonically to a partial pressure of about 11 torr. The Raman data for CO_2 appear to show steadily increasing partial pressure to about 7 torr while O_2 was present, then somewhat decreasing partial pressure. The initially present H_2O disappeared during the first 15 hours. An isotopic exchange route for its disappearance might be: $H_2O + T_2 = HTO + HT$; however, no production of HT was observed in

Fig. 3. Time evolution of the concentrations of T_2 , O_2 , and T_2O

Fig. 3. Time evolution of partial pressures of T_2 and O_2 . Note the break in slope at ~ 8 days, after which T_2 partial pressure continues to drop even though O_2 is completely depleted.

the Raman spectra, for which the detectability in this experiment would have been approximately 0.2 torr; no signal attributable to HTO was observed either (although is plausible that a HTO peak might be unresolved from T_2O under the present experimental conditions).

Raman spectra were acquired for several weeks following the O_2 disappearance, which is accompanied by a clearly reduced T_2 depletion rate (see Figs. 3-4). A single-exponential decay fitted to these late data yields a T_2 -depletion rate of 0.0045 hr^{-1} .

Following these Raman acquisitions, the final pressure in the Raman cell was determined, by expansion, to 415.4 torr. The final composition of this mixture, based on the observed and estimated Raman partial pressures and calculated ^3He generation from tritium decay, is reported in Table I. The sum of these partial pressures is 407.9 torr with an uncertainty as high as 11 torr due to unknown Raman calibrations for T_2O and other constituents, in excellent agreement with the Baritron measurement of total pressure.

B. Mass Spectroscopy

Immediately after the pressure measurement, the mixture was analyzed using a high-resolution mass spectrometer. The significant results, surmised by combining the best results from three separate analyses, are summarized in Table II.

Table II
Mass Spectroscopy Analysis of Final Composition

	^3He	HT	T_2	O_2	CO_2	Ar
Result, mol %:	0.44	0.485	3.53	None	1.3	1.40
Expected, mol %:	0.49	0.059	3.54	None	1.0	1.1

The mass-spectrometer analysis for ^3He , T_2 , Ar, and CO_2 is in good agreement relative with the values expected from calculation of tritium decay, Raman analyses, and noble-gas contents of air. The mass-spectrometer analyses disagree

significantly with the expected results for all hydrogen oxides (not shown), which is not unexpected as waters are extremely difficult to quantify with a mass spectrometer. They also appear to be in error for the trace amounts of HT (and DT, not shown) in this mixture. The agreement of ^3H e concentration with the expected value suggests that few, if any, tritium atoms were becoming so deeply bound in solid matrices (quartz or stainless-steel) that the decay-helium could not escape.

C. Subsequent Experiments

The unexplained disappearance mechanisms of T_2 after depletion of O_2 were further probed by two short experiments immediately following the removal of the moist-air mixture from the Raman cell. First, in conjunction with volume measurements using pure deuterium, deuterium at a pressure of 741.9 torr was left in the Raman cell for 64 hours. A subsequent Raman measurement of the cell contents revealed only pure deuterium and detected no DT from potential exchange with tritium sinks in the Raman cell (detection limit 0.16%), while a subsequent pressure measurement revealed no loss of deuterium (accuracy 0.05%). After evacuating this deuterium, a mixture of tritium (353.3 torr) and deuterium at a total pressure of 713.3 torr was prepared in the cell and observed by real-time Raman spectrometry over 3 days. The contents of the Raman cell and interconnections were then expanded into the evacuated manifold. The total of these gas quantities was at least 180 micromoles compared to 199 micromoles initially in the Raman-cell. This loss of less than 9.6% of the material can be compared to an expected loss at the final T_2 disappearance rate from the moist-air mixture over a comparable time, which would amount to 27%. Thus this experiment strongly suggests that the tritium disappearance in the air mixture, even after the disappearance of O_2 , is not due to mysterious tritium sinks in the Raman cell.

IV. CONCLUSION

Radiochemical reactions between pure tritium (T_2) and moist air have been examined using Raman and mass spectroscopy. The production of T_2O was unambiguously observed, as evidenced by a weak vibrational band at $\sim 2313\text{ cm}^{-1}$. Surprisingly, the radiochemical production of tritiated water did not occur in the expected 2:1 ratio but, rather, with the O_2 disappearing totally when the T_2 was only slightly over halfway depleted. After the disappearance of O_2 , the T_2 partial pressure continued to decrease, but at a slower rate. The initial water in the moist-air mixture disappeared totally after about 15 hours, with no concomitant production of HT. A small quantity of CO_2 was also detected, presumably resulting by radiochemically driven reactions with stainless

steel components. A subsequent deuterium-tritium exchange experiment in the same cell revealed no mysterious sinks for tritium.

These results strongly suggest that oxidation of tritium is not the sole mechanism of tritium depletion. Unambiguous Raman detection of T_2O in these experiments is heartening for understanding this oxidation, but the quantities of T_2O estimated from the Raman spectra of about 10 torr, combined by the lack of leveling of Raman signals upon reaching dew point, are 10-20 times lower than expected from stoichiometric oxidation of T_2 . Similarly the continued depletion of tritium following the disappearance from O_2 from the mixtures at about 200 hours also signifies an additional mechanism for tritium depletion in these mixtures. One possible explanation might be the initial peroxidation of tritium according to $\text{T}_2 + \text{O}_2 = \text{T}_2\text{O}_2$, followed by subsequent oxidation of tritium by $\text{T}_2\text{O}_2 + \text{T}_2 = 2\text{T}_2\text{O}$. Although the mass-spectrometric analyses yielded nonreproducible signals at mass 36 and especially mass 38, (which could not be attributed to F_2 as the signal at mass 19 was nonexistent), the general unreliability of the mass spectrometer for all of the hydrogen oxides implies neither support nor denial for this potential mechanism. Moreover, the benign results of the subsequent deuterium/tritium exchange experiment prove that no mysterious sinks for tritium exist in this Raman cell. Thus, tritium depletions, both at a moderate rate (but less than stoichiometric for T_2O formation) while O_2 is present and at a somewhat slower rate after the disappearance of O_2 from the mixture, appear to be intrinsic to the tritium/air mixtures.

The radiochemical reaction mechanisms underlying this experiment, as well as the dependence of tritium depletion rates on total pressure, relative tritium concentration, and cell geometry still need to be explored in further experiments.

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