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Authors

Fee, Darrell C.
Markowitz, Samuel S.

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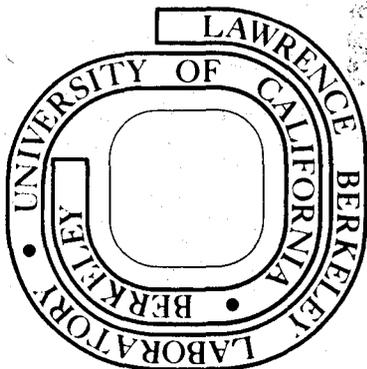
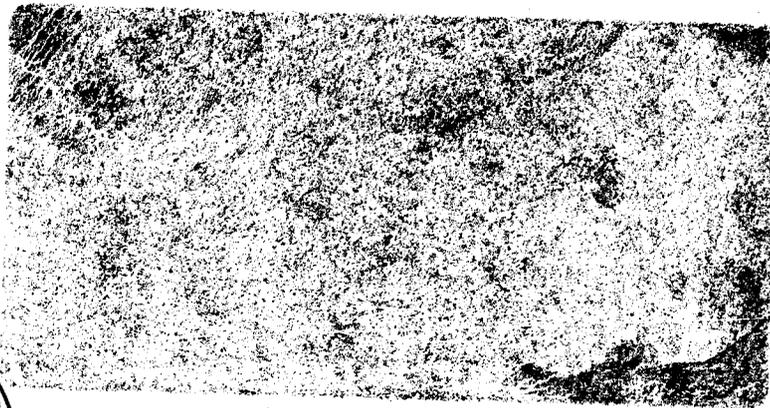
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RECOIL TRITIUM REACTIONS WITH ALKENES:

FORMATION OF "POLYMER-T"*

Darrell C. Fee[†] and Samuel S. Markowitz

Department of Chemistry and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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ABSTRACT

Recoil tritium atom addition to an alkene creates an alkyl-t radical. The alkyl-t radical may add to the alkene initiating a tritiated radical chain. These high molecular weight tritiated chain hydrocarbons are recovered and analyzed as "polymer-t". A method of "polymer-t" recovery is described and evaluated. The efficiency of recovery of "polymer-t" is strongly dependent upon the scavenger used. With SO₂ scavenging, a higher percentage of the "polymer-t" is recovered than with O₂ scavenging. With SO₂ scavenging the recovery of "polymer-t" from T + alkene reactions is 75 to 85% complete. The dependence of "polymer-t" yield on the presence of scavengers (SO₂ or H₂S) indicates that the formation of "polymer-t" is a low-energy, radical process.

INTRODUCTION

Recoil tritium reactions have now been observed with over one hundred parent molecules [1-3]. The main reaction channels observed for recoil tritium atoms are: (1) Abstraction to form HT. (2) T-for-H substitution to form a tritiated parent molecule. (3) Addition to a double bond to form an excited alkyl-t radical. The excited alkyl-t radical, unless collisionally stabilized, may undergo unimolecular decomposition/isomerization [4-5].

Collisionally stabilized alkyl-t radicals are also capable of further reaction. The concentration of radiolysis produced radicals (formed by the recoiling ions following the $^3\text{He}(n,p)\text{T}$ reaction) is kept low to make radical-radical reactions negligible. Therefore, the only reactions of collisionally stabilized alkyl-t radicals in ^3He -hydrocarbon systems are: (i) Abstraction of a hydrogen atom to form an alkane-t species. (ii) Addition to the double bond of the parent hydrocarbon initiating a tritiated radical chain. The chain termination step is abstraction of a hydrogen atom. Tritiated dimers have been observed by radio-gas-chromatography [6,7].

In the typical gas phase recoil tritium experiment, ^3He and the parent compound are prepared and neutron irradiated in a 1720 Pyrex capsule (2 cm o.d., 14 to 18 ml internal volume). The capsule is then mechanically crushed in the helium flow stream of a gas chromatograph. The column effluent is mixed with a counting gas and the radioactivity (of the tritium) measured as the mixture flow through an internal proportional counter. Tritiated dimers (and higher tritiated "polymers") usually cannot be analyzed routinely by radio-gas-chromatography. Often the retention times of these materials are extremely long and peak shapes are unusually poor.

Tritiated products not eluted in the normal forward flow of the radio-gas-chromatographic analyses have been recovered and monitored as "polymer-t" [8]. While the "polymer-t" data does not indicate the chemical composition of the tritiated products, it does allow crude separation by volatility. Low (molecular weight) "polymer-t" is defined as tritiated products that are back-flushed from the chromatographic columns. Medium "polymer-t" is defined as tritiated products that are washed from a stainless steel capillary tube (operated at 25°C) connecting the sample crusher to the chromatographic column. High "polymer-t" is defined as tritiated products that are washed from the walls of the sample capsule in which the recoil tritium reaction took place. Low "polymer-t" is the most volatile "polymer-t" category. Low "polymer-t" is carried from the sample crusher to the chromatographic column by the helium flow stream. In contrast, high "polymer-t" is not volatile in the helium flow stream. High "polymer-t" remains in the sample crusher (on the walls of the sample capsule in which the recoil tritium reaction took place).

Quantitative measurement of "polymer-t" is made by liquid scintillation techniques. The number of tritium atoms in any one "polymer-t" category, N_p , may be compared to the number of tritium labeled molecules in the i th radio-gas-chromatographic peak, N_i , by

$$A_i = \lambda N_i E V F^{-1} \quad (1)$$

Where A_i is the experimentally determined area of the i th radioactivity peak (counts), λ is the nuclear decay constant for tritium (sec^{-1}), E is the detection efficiency of the counter for tritium, V is the active volume of the counter (ml) and F is the flow rate of the counting gas through the counter (ml sec^{-1}). The calculation of N_i is made from Equation (1) after all other

variables are experimentally determined. Changes in the N_p/N_i ratio with changes in phase, scavenger, or isotope (D in place of H in the parent compound) have provided insights into recoil tritium reaction mechanisms [9-12].

Recently we reported scavenger effects on the "polymer-t" yield in T + cyclohexene reactions [12]. A glaring inconsistency developed in the "polymer-t" data when H_2S was employed as scavenger. The rate constant at 25°C for the reaction of alkyl radicals with H_2S (via H atom abstraction to form an alkane) is larger than with alkenes by several order of magnitude [12]. Consequently, with H_2S scavenging, all cyclohexyl-t radicals from T + cyclohexene reactions (at 25°C) should be monitored as cyclohexane-t. In H_2S scavenged T + cyclohexene reactions, the expected increase in the cyclohexane-t should be accompanied by an equal decrease in the "polymer-t" yield. Experimentally the decrease in polymer-t yield was only 48% of the increase in the cyclohexane-t yield. We decided to re-examine critically the method of recovery and analysis of "polymer-t".

EXPERIMENTAL

The samples were prepared in 1720 Pyrex capsules using vacuum line techniques similar to those previously described [13]. More details of sample preparation are given elsewhere [14]. The 3He (Mound Laboratories) was certified as 99.7 mole % 3He with a tritium content of 1.0×10^{-11} mole %. A standard radio-gas-chromatographic analysis [15] of an unirradiated aliquot of 3He containing at least twice the moles normally sealed in the 1720 Pyrex capsules showed no measurable tritiated contaminant. The 3He was used directly from the Mound Laboratories' container without further purification. All other materials used were research grade. All irradiations were made in the Berkeley Campus Nuclear Reactor. Irradiations of 25°C were made in the Lazy Susan facility for 10 min at a flux of 3.8×10^{11} n cm⁻² sec⁻¹. Irradiations

at $135 \pm 0.5^\circ\text{C}$ were made in the Hohlraum in a specially designed irradiation container described elsewhere [16]. The irradiations at 135°C were for 8.0 hours at a flux of $3.9 \times 10^8 \text{ n cm}^{-2} \text{ sec}^{-1}$. Radiation damage due to the recoils following the $^3\text{He}(n,p)\text{T}$ reaction was less than 1%.

The samples were analyzed with a radio-gas-chromatographic technique detailed elsewhere [15]. "Polymer-t" was recovered in 10 ml toluene fractions in standard liquid scintillation vials. Added to this was a 10 ml aliquot of a standard liquid scintillator solution containing 4 gm POP (2,5 diphenyloxazole) and 0.1 gm dimethyl POPOP (1, 4-di-(2-[4-methyl-5-phenyl oxazolyl]-benzene)) per liter of toluene. Corrections for sample quenching and determinations of the absolute counting efficiency were made by the external standard ratio method [17] using a Nuclear-Chicago Mark II liquid scintillation spectrometer. All data reported represent the average of the yields from two identical samples. The yields of products from identical samples agreed to within 5% for radio-gas-chromatographic data and to within 10% for "polymer-t" data.

RESULTS AND DISCUSSION

A. Low (Molecular Weight) "Polymer-t"

Low "Polymer-t" was back-flushed from the chromatographic column. Low "polymer-t" is collected in toluene when the reversed flow from the column is bubbled through a toluene trap. The trap itself was a liquid scintillation vial in which the low "polymer-t" from that particular analysis would be counted. This prevented possible loss of low "polymer-t" during mechanical transfer of the toluene. The reversed flow rate through the column was the same as the forward flow rate. The back-flushing and trapping period was routinely twice the time of forward flow.

The efficiency of the toluene trap for recovery of low "polymer-t" was measured with a second toluene trap in series in the flow stream. The trapping efficiency was $94 \pm 1\%$. The trapping efficiency was the same whether the trap was operated at 0°C or 25°C . The overall efficiency of recovery of low "polymer-t" from the chromatographic column was measured. A second back-flushing period starting with a new toluene trap showed that $99 \pm 1\%$ of the low "polymer-t" was collected in the first back-flushing period.

B. Medium "Polymer-t"

Medium "Polymer-t" is washed with 10 ml of toluene from a 10 ft section of 1/16-inch o.d. stainless steel capillary tubing. The capillary tubing is immediately downstream from the sample crusher. The toluene (and medium "polymer-t") was collected directly in a liquid scintillation vial. The efficiency of the recovery of medium "polymer-t" was measured. A second flushing of the capillary tubing with 10 ml of toluene revealed that $99 \pm 1\%$ of the medium "polymer-t" was collected in the first flushing. The capillary tubing was routinely flushed with acetone after the recovery of medium "polymer-t" to prevent any carry-over of trace activity from one analysis to another.

Medium "polymer-t" was apparently migrating down the capillary tubing and onto our arrangement of gas chromatographic columns [15]. We routinely employed three columns in series. The order of the columns in the series was changed during the radio-gas-chromatographic analysis. A system of 4-way valves was required to change the order of the columns. When the cool tube eluted directly into the system of 4-way valves, over 90% of the low "polymer-t" was back-flushed

from the first column (during sample injection [15]) downstream from the capillary tubing. A check of calibrated retention times showed that the low "polymer-t" from columns other than the first column downstream was spurious. All radio-gas-chromatographic peaks would be eluted from those columns in the normal forward flow analysis. This spurious low "polymer-t" was reduced to essentially zero when a six inch column (1/4-inch o.d. copper tubing) of 60/80 mesh glass beads was placed immediately downstream from the capillary tubing but before the first 4-way valve. A toluene flushing of a second capillary tube between the glass bead column and the first 4-way valve showed that medium "polymer-t" did not migrate through the glass bead column (operated at 25°C). Medium "polymer-t" was routinely back flushed from the glass bead column. The reported medium "polymer-t" values represent the sum of contributions from the capillary tubing and glass bead column. Low "polymer-t" was routinely back flushed only from the first column (during sample injection downstream from the glass bead column).

C. High "Polymer-t"

High 'polymer-t' is washed from the walls of the sample capsule in which the recoil tritium reaction took place. The fragments of 1720 Pyrex glass from the crushed sample capsule were poured from the sample crusher directly into a standard paper Soxhlet extraction thimble. The thimble was then placed into a Soxhlet extractor. The 130 ml of toluene to run the extractor was routinely flushed through the sample crusher directly into the Soxhlet extractor. Thus, high "polymer-t" was also recovered from the internal walls of the sample breaker. The distribution of high "polymer-t" between

1720 Pyrex fragments and the internal walls of the sample cursher was determined. The internal walls of the sample crusher were washed with successive 10 ml aliquots of toluene. Each washing was collected directly in a liquid scintillation vial. The high "polymer-t" from the internal walls of the sample crusher was less than 10% of the total high "polymer-t". The high "polymer-t" from the internal walls of the sample crusher was concentrated in the first 20 to 30 ml collected and decreased from the first 10 ml to an insignificant level after 100 ml.

The Soxhlet extraction process was routinely carried on for 24 hours. The extraction thimble and 1720 Pyrex fragments were then removed. The Soxhlet extractor was then allowed to go through several more cycles before it was stopped again with the majority of the toluene in the upper part of the extractor. The volume of the toluene in the upper part of the extractor was measured and a 10 ml aliquot taken. All of the toluene in the lower part of the extractor was collected in 10 ml aliquots in liquid scintillation vials. The bottom part of the Soxhlet extractor was then routinely rinsed with 10 ml of toluene and this rinse also collected and counted. This rinse was less than 1% of the total high "polymer-t" recovered. The Soxhlet extractor was then carefully washed with soap and water, then with acetone. A "blank" extraction on a empty Soxhlet extraction thimble showed no carry over of activity from one analysis to another.

The efficiency of the recovery of high "polymer-t" was measured. The extraction thimble and 1720 Pyrex fragments from a completed extraction were transferred to another Soxhlet extractor, fresh toluene was added and another

24 hour extraction was carried out. This showed that $97 \pm 2\%$ of the high "polymer-t" was recovered in the first 24 hour extraction. The high "polymer-t" recovered by the Soxhlet extraction process was tritiated material which came to rest on the interior wall of the 1720 Pyrex capsule. No high "polymer-t" resulted from tritons (tritium ions) recoiling into the 1720 Pyrex capsule wall [18] and subsequently being leached out by the Soxhlet extraction process. No high "polymer-t" (and no low or medium "polymer-t") was found when ^3He was irradiated in the 1720 Pyrex capsule without an accompanying hydrocarbon. No "polymer-t" was found from irradiated samples containing only ^3He and H_2S , O_2 , or SO_2 scavengers and no hydrocarbon. The accompanying radio-gas-chromatographic analysis of these four conditions (^3He alone, $^3\text{He} + \text{H}_2\text{S}$, $^3\text{He} + \text{O}_2$, $^3\text{He} + \text{SO}_2$; all samples irradiated) showed no radioactive peaks except for $^3\text{He} + \text{H}_2\text{S}$. The $^3\text{He} + \text{H}_2\text{S}$ samples exhibited an HT peak; presumably from recoil tritium atom abstraction reactions with H_2S .

The data taken with this method are shown in Table 1. With H_2S scavenging, the tritiated radicals formed by T + cyclohexene reactions are assumed to react with H_2S (to give products monitored by radio-gas-chromatography) rather than with cyclohexene (to give "polymer-t"). With O_2 or SO_2 scavenging, the tritiated radicals are assumed to react with O_2 or SO_2 rather than with cyclohexene [12]. The identity of the O_2 or SO_2 scavenged species is unknown. The O_2 and SO_2 scavenged tritiated species are monitored as "polymer-t". Therefore, a decrease in the sum of gas phase product yields from H_2S to O_2 or SO_2 scavenging should be marked by an equal increase in "polymer-t". Two things should be noted: (a) No correction was necessary for ^{35}S activity (from the $^{34}\text{S}(n,\gamma)^{35}\text{S}$ reaction) which could be included in our measurements as

^{35}S was incorporated into the "polymer-t". Even with the highest SO_2 or H_2S pressures, the total ^{35}S activity is less than 1% of the "polymer-t" activity.

(b) In contrast to previously reported data [8-12], corrections for sample quenching were made for the data in Table 1. The previously held assumption was that only trace amounts of radioactive material was being recovered so sample quenching was not important. This assumption was invalid. For example, the increase in total "polymer-t" yield when corrections are made for quenching (versus assuming a constant efficiency of counting for all sample vials) ranged from 10 to 30 percent for the T + cyclohexene data. The high "polymer-t" samples were quenched the most.

As shown by the T + cyclohexene reaction data in Table 1, 85% of the "polymer-t" expected from material balance arguments is recovered with SO_2 scavenging versus 35% with O_2 scavenging. Similarly for the T+ 1-butene reaction data in Table 1, 75% of the "polymer-t" expected from material balance arguments is recovered with SO_2 scavenging versus 15% with O_2 scavenging. The increase in "polymer-t" yield from O_2 to SO_2 scavenging is in the high "polymer-t" grouping. This may indicate that the SO_2 scavenged species are more soluble in toluene than the O_2 scavenged species. The difference in efficiency of "polymer-t" recovery with SO_2 scavenging for cyclohexene versus 1-butene (85% versus 75%) may indicate that the efficiency of the recovery process depends slightly upon the chemical nature of the "polymer-t".

In addition to the increase in high "polymer-t" yield with SO_2 versus O_2 scavenging, Table 1 also shows a decrease in the low and medium "polymer-t" yield with SO_2 versus O_2 scavenging. A shift in "polymer-t" yield from low to high (molecular weight) "polymer-t" with SO_2 versus O_2 scavenging has also

been reported for the T + trans-2-butene system [11]. The lowered "polymer-t" volatility with SO₂ scavenging is consistent with the expected formation of scavenged species of higher molecular weight and/or lowered volatility with SO₂ than O₂. The relative abundance of the "polymer-t" volatility groupings is also affected by temperature. In O₂ scavenged T + cyclohexene reactions at 135°C [5], low and medium "polymer-t" account for nearly 70% of the total "polymer-t" recovered. The temperature effect on "polymer-t" formation is probably slight. The temperature effect on "polymer-t" distribution may arise from heating the sample crusher to 135°C (for samples irradiated at 135°C) versus 25°C (for samples irradiated at 25°C). The increased temperature when the sample was crushed may increase the volatility of "polymer-t".

We conclude that: (1) The efficiency of recovery of "polymer-t" is strongly dependent upon the scavenger used. With SO₂ scavenging, a higher percentage of the "polymer-t" is recovered than with O₂ scavenging. (2) The recovery and analysis of "polymer-t" from T + alkene reactions by the method described may be only 75 to 85% complete. Although the recovery of "polymer-t" may not be complete, the large amount of "polymer-t" recovered supports the proposed mechanism of "polymer-t" formation. The dependence of "polymer-t" yield on the presence of scavengers (SO₂ and H₂S) indicates that the formation of "polymer-t" is a low-energy, possibly thermal, radical process.

FOOTNOTES AND REFERENCES

*Work performed under the auspices of the U. S. Atomic Energy Commission.

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Table 1. T + ALKENE REACTION DATA^a AT 25°C

| Alkene | Scavenger | "Polymer-t" Yield | | | | Cyclohexane-t Yield | Sum of Gas Phase Product Yields ^b |
|-------------|------------------|-------------------|--------|------|-----|------------------------|--|
| | | Low | Medium | High | Sum | | |
| Cyclohexene | H ₂ S | 2 | 2 | 34 | 38 | 109 | 201 |
| | O ₂ | 4 | 11 | 79 | 94 | 1 | 48 |
| | SO ₂ | 2 | 4 | 170 | 176 | 1 | 43 |
| | | | | | | Butane-t Yield | |
| 1-Butene | H ₂ S | 8 | 3 | 11 | 22 | 135 | 304 |
| | O ₂ | 22 | 5 | 18 | 45 | 3 | 148 |
| | SO ₂ | 4 | 3 | 13 | 137 | 4 | 150 |

^aTritiated product yields relative to yield of tritiated parent compound as 100.

^bSum of all tritiated product yields monitored by radio-gas-chromatography except HT_i and the tritiated parent compound.

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UNIVERSITY OF CALIFORNIA
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