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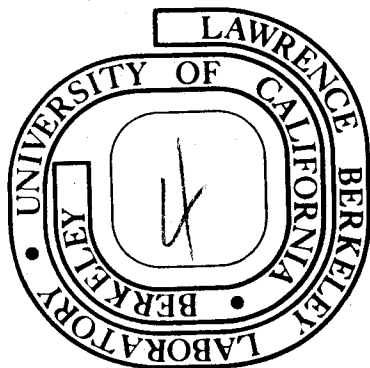
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ION-MOLECULE REACTIONS IN RECOIL TRITIUM CHEMISTRY*

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Sir: The possibility of ion-molecule reactions in recoil tritium chemistry has been dismissed^{1,2} through application of the adiabatic principle.³ However, the energy defect was incorrectly evaluated from the unperturbed energy levels of the isolated particles.⁴⁻⁶ Experimentally, Rowland and co-workers have established an upper limit of 10% for the contribution of excited electronic states in T-for-H substitution.⁷ Experimentally, the yield of HT is higher in the presence of helium (versus other noble gases). To explain this, Seewald and Wolfgang⁸ proposed that 6% of the total tritium reacted as unneutralized T⁺ because of the high ionization potential of helium while Urch and Malcolm-Lawes^{9,10} proposed greater stabilization of highly excited HT by helium.

Unexplained by Urch and Malcolm-Lawes is the higher yield of "polymer-t" accompanying the higher HT yield in helium (versus xenon) moderated T + cyclohexene reactions.¹¹ "Polymer-t is tritiated material that is backflushed from the chromatographic columns and washed from the walls of the sample capsule in which the recoil tritium reaction took place.^{12,13} Recently, "polymer-t" has been characterized by Filatov and co-workers using thin layer chromatography.¹⁴ Table I shows some "polymer-t" data. Irradiations and sample analysis are discussed

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elsewhere.^{15,16} The key feature of Table I is that the "polymer-t" yield is non-zero with H₂S scavenging. The "polymer-t" yield was zero in an irradiated blank containing ³He and scavenger but no hydrocarbon. The ³⁵S activity (due to ³⁴S(n,γ) ³⁵S from H₂S) is less than 5% of the "polymer-t" yield with H₂S scavenging. Filatov, et al., showed that "polymer-t" in unscavenged T + cyclohexene reactions was formed by chain addition initiated by cyclohexyl-t radicals. However, calculations show that radical-molecule (and radical-radical) routes to "polymer-t" formation are eliminated by H₂S, which donates a hydrogen atom to the radical. Rate constants used (units of cm³ mole⁻¹ sec⁻¹) were for methyl radicals reacting with H₂S¹⁷ (3.0 × 10⁹), with trans-2-butene¹⁸ (for cyclohexene, 2.6 × 10⁵), and with methyl radicals¹⁹ (2.4 × 10¹²). In the H₂S scavenged T + cyclohexene system, the estimated steady state concentration of: (1) tritium labeled radicals (chiefly cyclohexyl-t radicals, see Table I) is 7 × 10⁻¹⁹ moles cm⁻³; (2) unlabeled radicals (formed at one ion pair per 30 eV energy deposited by the ³He(n,p)T reaction) is 6 × 10⁻¹⁴ moles cm⁻³. The rate of reaction of tritiated radicals with H₂ is estimated to be three orders of magnitude larger than the rate of reaction of tritiated radicals with either: (1) cyclohexene or (2) unlabeled radicals. Experimentally, the scavenger plateau of the cyclohexane-t yield¹⁵ shows that cyclohexyl-t radicals react solely with H₂S rather than cyclohexene or unlabeled radicals in competition with H₂S.

The "polymer-t" yield not scavengeable by H₂S is 6% of the total yield of tritiated products (HT + parent-t + other tritiated gas phase products + "polymer-t") in T + cyclohexene reactions (4% in T + i-butene reactions). We propose that the "polymer-t" yield that is unscavengeable by H₂S results from ion-molecule processes. Typical ion-molecule reac-

tion rate constants²⁰ are 10^{14} to 10^{15} $\text{cm}^3 \text{mole}^{-1}$. These rate constants are larger by two orders of magnitude than radical-radical rate constants. In addition, tritiated ion chains, unlike tritiated radical chains, are not terminated by reaction with H_2S .²⁰

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Table I. TRITATED PRODUCT YIELDS^a FROM T + ALKENE REACTIONS AT 25° C

Parent	Scavenger	Yields		
		"polymer-t"	alkane-t	gas-phase-t ^b
Cyclohexene ^c	H ₂ S	37	109	200
(alkane-t = cyclohexane-t)	none	75	32	96
	SO ₂	174	1	44
1-Butene ^d	H ₂ S	22	135	304
(alkane-t = butane-t)	none	61	21	195
	SO ₂	139	4	150

^a Tritiated product yields relative to yield of tritiated parent compound was 100. Results of two samples that agreed to within 10%.

^b Sum of all tritiated products monitored by radio-gas-chromatography except HT and the tritiated parent compound. For material balance of products with a radical intermediate, the decrease in gas phase product yields between H₂S and SO₂ scavenger should be accompanied by an identical increase in the "polymer-t" yield. The smaller change in the "polymer-t" yield indicates that "polymer-t" recovery is $((174-37)/(200-rr)) \times 100\% = 88\%$ complete for T + cyclohexene reactions (77% for T + 1-butene).

^c Sample composition (cm Hg): ³He 1.6, cyclohexene 5.6, (6 mole % scavenger).

^d Sample composition (cm Hg); ³He 1.7, 1-butene 14. (7 mole % scavenger).

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