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SULFUR DIOXIDE AS A RADICAL SCAVENGER IN ALKENE SYSTEMS

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SUMMARY

The comparative efficiency of SO_2 and O_2 as radical scavengers has been determined in the T + cyclohexene, T + transbutene, and T + n-butane gas phase systems. T was produced by recoil in the $^3\text{He}(n,p)\text{T}$ reaction. O_2 , the only scavenger currently in use in T + alkene systems, causes an anomalous increase in the butadiene-t yield from T + cyclohexene reactions. All other tritiated products from cyclohexene and transbutene + T reaction show similar scavenging trends. The use of SO_2 as a radical scavenger may be advantageous in some alkene systems although SO_2 fails to eliminate all thermal contributions to the HT yield in the T + n-butane system.

Many recoil tritium experiments have used scavengers to remove thermalized tritium atoms and radical intermediates from the system before such species yield products which might be confused with high energy tritium reactions [1]. Oxygen [2], iodine [3], bromine [3], deuterated ethylene [4], nitric oxide [5], and iodine halides [6] have been used in gas phase experiments. All of these satisfy some of the criteria for a good scavenger proposed by Hawke and Wolfgang [6], namely

- 1) a scavenger must react avidly with the atoms and radicals to be removed, preferably with a collision efficiency near unity. It may then be used in sufficiently low concentrations so as not to interfere with the hot or

other primary processes being studied. We are interested in recoil tritium reactions with alkenes. Deuterated ethylene is thus eliminated by this criteria since its scavenging ability is of the same order of magnitude as other alkenes [7].

2) a scavenger should be inert with respect to the bulk reagent. For alkene systems, this eliminates iodine, bromine, and the iodine halides since they would undergo rapid addition to the double bond.

3) products of the scavenging reaction should not react further, or if they do, such reaction should be controllable. In the recoil tritium-trans-butene system, the presence of nitric oxide increased the 1-butene-t yield by 100%, presumably through a reversible reaction with sec-butyl-t radicals [8]. Thus nitric oxide is an unreliable scavenger for alkenes.

4) a gas phase scavenger must have an adequate vapor pressure at the temperature in question. Oxygen, the only reported scavenger left for alkene systems, readily satisfies this criterion.

5) Furthermore it is highly desirable, but not always essential that the scavenged species be detectable. The peroxy radicals formed from

are not readily assayed in the conventional radiogas chromatographic methods used for recoil tritium experiments. In addition, the peroxy radicals may react further with either the bulk reagent or other radicals in the system. As yet, there is no evidence that such further reaction results in products which might be mistaken for the yield of a hot reaction.

We report here a comparison between oxygen and sulfur dioxide as scavengers for recoil tritium-alkene systems. Sulfur dioxide was selected since its reaction with radicals in other systems was known [9]. The experimental procedure employed was similar to that described previously for sample preparation and analysis of gas phase tritium labeled products [10], and recovery of "polymer-t" [11]. The irradiations, made in 1720 pyrex capsules, were for 10 min at a flux of 2.7×10^{11} n/cm² sec. Radiation damage due to the recoils following the $^3\text{He}(n,p)\text{T}$ reaction was less than 1%. All data reported represents the average of the yields from two identical samples which agreed on major products to within 3% on the C₄ runs and to within 5% on C₆ runs. No correction has been made for "wall HT" [12].

The efficiency of a scavenger is determined by the dependence of various products on scavenger concentration. The yield of products formed solely by hot reactions will remain unchanged over a wide range of scavenger concentrations. The yield of products formed by both thermal and hot processes will decrease rapidly with the addition of scavenger until a plateau is reached where the yield is relatively insensitive to scavenger concentration. In this region, all thermal reactions, except with the scavenger, have presumably been suppressed and the yield is due entirely to hot reactions [6].

In the T + cyclohexene system, the scavengeable thermal reaction product is cyclohexane-t which results largely from thermal addition of T to the double bond to form a cyclohexyl-t radical. This radical then abstracts a hydrogen from the bulk system to form cyclohexane-t. Ethylene-t and butadiene-t are high energy products from the unimolecular decomposition of excited cyclohexene-t formed by direct substitution [13]. The yields of these products for

both O_2 and SO_2 scavenger are shown in fig. 1. The sharp drop in cyclohexane-t yield is the same for both O_2 and SO_2 . The small drop in the ethylene-t yield is the same for both O_2 and SO_2 and indicates a small thermal route in ethylene-t formation. The butadiene-t yield is constant with SO_2 scavenging but increases by 50% with O_2 scavenging! This anomalous increase in butadiene-t yield with O_2 scavenging is similar to an anomalous increase in the ethylene-t yield with O_2 scavenging that was reported by Urch and Welch in the T + ethane system [3].

This anomalous ethylene-t increase was explained by Baker and Wolfgang [4]. Apparently, in the absence of O_2 , radiation produced H atoms were being scavenged by the ethylene-t formed by hot tritium reactions. This reduced the ethylene-t yield in unscavenged systems. When O_2 was added, the radiation produced H atoms were scavenged by the more efficient O_2 and the ethylene-t yield rose to its "hot" value. A similar explanation is unfeasible here. The bulk of the system is cyclohexene which would scavenge any radiation produced H atoms [14]. Another anomalous effect in the cyclohexene + O_2 system is that when samples were irradiated and analyzed less than two weeks after they were prepared (as in data reported here) O_2 uniformly reduced the cyclohexane-t yield. However we found oxygen to be an unreliable scavenger in samples which had been stored 3-4 months. Apparently oxygen failed due to reaction with cyclohexene. The rate of cyclohexene hydroperoxide formation is non-negligible at room temperature and increases with temperature. In addition a pyrex glass surface has a catalytic effect on the initial stages of the reaction [15]. This may rule out simultaneously raising the vapor pressure of cyclohexene by elevating the temperature and employing O_2 as a scavenger.

The comparison of O_2 and SO_2 was also made in the trans-butene + T system. As shown in fig. 2, the yield of butane-t, a product analogous to cyclohexane-t, was sharply reduced on the addition of both O_2 and SO_2 . All other products exhibited the same yields for both O_2 and SO_2 scavenging including a 50% decrease in the 1 butene-t yield. The anomalous increase in the 1 butene-t yield with NO as scavenger was duplicated in this laboratory.

Sulfur dioxide thus compares favorably with oxygen in some alkene systems and is superior in others. Sulfur dioxide has an adequate vapor pressure of over two atmospheres at room temperature [16]. Similar to oxygen scavenging, SO_2 scavenged species of the form $R-SO_2$ and HSO_2 are a) capable of further reaction. No problems of this sort are apparent in the SO_2 data to date. b) undetected in conventional analysis of gas phase products. While the "polymer-t" data does not indicate the chemical composition of the tritiated products, it does allow crude separation by volatility. Light "polymer-t" is backflushed from the chromatographic columns. Medium "polymer-t" is washed from a 10 ft. cool tube connecting the sample breaker to the chromatographic columns. Heavy "polymer-t" is washed from the walls of the capsule in which the recoil tritium reaction took place [11]. The relative abundance of activity in each volatility grouping changes with the scavenger employed. In the T + trans-butene system, for example, the "polymer-t" yield was distributed: 75% in the light and 18% in the heavy groupings for unscavenged samples; 65% in the light and 22% in the heavy groupings for O_2 scavenged samples; 4% in the light and 95% in the heavy groupings for the SO_2 scavenged samples. The lowered polymer-t volatility with SO_2 scavenging is consistent with the expected formation of scavenged species of higher molecular weight and/or lower volatility with SO_2 .

than O_2 . No correction was necessary for ^{35}S activity (from the $^{34}S(n,\gamma)^{35}S$ reaction) which could be included in our measurements as $^{35}SO_2$ incorporated into the "polymer-t". Under the most extreme conditions, the total ^{35}S activity is less than 1% of the "polymer-t" activity.

We have also compared the scavenging ability of SO_2 and O_2 in an alkane system where hydrogen abstraction to form HT is the low energy reaction. The most stringent test of scavenging efficiency was conducted in a highly moderated system, where the chance of high energy tritium atom colliding with a reactant molecule at a given energy decreases. This results in an increased number of thermalized tritium atoms which would contribute to the yield of a given product. Consequently the required level of scavenger efficiency is higher when moderator is present [6]. Figure 3 shows the effects of SO_2 and O_2 on the HT yield for on 86% Ne moderated T + n-butane system.

Oxygen scavenging of this system with 93% helium moderator has been previously reported by Rosenberg and Wolfgang [17]. Our data reproduces the reported scavenging plateau, but shows a different HT/ C_4H_9T ratio along the plateau and especially at the zero scavenger intercept. This difference can be attributed to the different moderators used. We selected Ne instead of He moderator to avoid complications from ion-molecule reactions which have been found in He moderated systems [13,18]. The SO_2 data points show no scavenger plateau. In addition all of the thermal tritium atoms are not being removed by SO_2 since the HT yield is higher for the SO_2 than for the O_2 scavenged samples. These trends are also seen in the data from unmoderated T + n-butane reactions shown in fig. 4. The difference in scavenging efficiency observed here can be attributed to the large difference in collisional efficiency between O_2 and SO_2 for reaction with thermal tritium atoms.

The measured rate constants for reactions (1) [19] and (2) [20] for protium in place of tritium show a 10^5 preference for O_2 over SO_2 .

We conclude that while SO_2 is not a good scavenger in alkanes it compares favorably with O_2 as a scavenger for alkenes. The use of SO_2 as a scavenger may be advantageous in alkenes since O_2 , the only other scavenger available, shows some anomalous effects in cyclohexene.

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FIGURE CAPTIONS

Fig. 1. Curves of T + cyclohexene system scavenged with SO_2 or O_2 . Product yields are listed relative to cyclohexene-t yield as 100. The zero scavenger data point and the 5 mole % scavenger data point have been connected with a line for clarity. We do not mean to imply that the variation of yield with added scavenger is linear in this region.

Fig. 2. Curves of T + trans-butene system scavenged with SO_2 or O_2 . The ordinate gives the butane-t yield relative to the transbutene-t yield as 100.

Fig. 3. Curves of T + n-butane system scavenged with SO_2 or O_2 and moderated with 86 mole % Ne. The ordinate gives the HT yield relative to the n-butane-t yield as 100.

Fig. 4. Curves of T + n-butane system scavenged with SO_2 or O_2 . The ordinate gives the HT yield relative to the n-butane-t yield as 100.

XBL714-3238

Fig. 1

XBL 714 -3239

Fig. 2

Moles scavenger + moles butane

XBL714 - 3237

Fig. 3

XBL 714-3240

Fig. 4

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