were detected, these reactions were conducted in triplicate, and Table 1 records the averages of the three runs. The raw data in the Additional Material show satisfactory (± 5% or less) agreement from run to run.

At 0.1 M (entry 4), the reaction of **11a** goes to complete conversion and provides a high yield of reduced product **14a** (95%) along with a trace of ketone **15** (2%). At 0.01 (entry 5), the conversion is again complete and yields of **14a** and **15** are now 73% and 8%, respectively. However, as the reaction is diluted to 0.005 M (entry 6), the conversion of **11a** becomes incomplete (42% recovery), while the yield of **14a** declines to 28% and that of ketone **15** increases to 16%. Finally, at 0.001 M (entry 7), the yield of recovered **11a** is still substantial (43%), while the amount of ketone **15** has stayed the same (16%) and the amount of the cyclized product **14a** dropped to only 1%. A significant amount (40%) of the initial mass balance is unaccounted for in the three experiments at this concentration.

At first glance, the appearance of significant amounts of ketone **15** in the experiments with **11a** at lower concentrations seems to support the fragmentation of radical **13a** to release an acyl radical **16a**. However, the ratios of **15**/**14a** do not fit well with the standard model of competing unimolecular (fragmentation) and bimolecular (reduction) reactions in Figure 4. For example, the 10-fold dilution in going from entry 4 to entry 5 should have resulted in a **15**/**14a** ratio about two times higher then was observed. In contrast, the small change in concentration going from entry 6 to 7 now results in an inordinately large increase in this ratio.

We feel that the results in Table 1 with **11a** might be better accommodated by an oxidation pathway for conversion of radical **13a** to ketone **15** via cation **17a**. Since the nature of the oxidant is not known, it is not possible to interpret the concentration dependence of the product ratios. However, the trends of decreased conversions, decreased yields and lost mass balance are not uncommon in such radical oxidation reactions, especially those run under ostensibly reducing conditions [9]. The oxidation step may be inefficient and is almost surely a chain-breaking event. Thus, when the rate of the unspecified oxidation reaction(s) begins to exceed the rate of reduction of radicals **13a** by tin hydride, the whole process begins to break down, so low conversions and yields result.

AIBN has been suggested to be an oxidant in related reactions, [9,33] so we conducted a series of individual cyclizations of **11a** at 0.01 M with increasing amounts of AIBN. The results of these experiments are summarized in Table 2. If AIBN is acting as an oxidant, then the yield of **14a** should decrease and **15** should increase as the concentration of AIBN increases. These trends were not observed. Instead, the yield of **14a** stayed about constant, while the yield of **15** decreased by a small amount. These experiments do not support the active role of AIBN as anything other than a standard radical chain initiator.

**Table 2: Effect of AIBN Concentration on Product Yields in Reaction of 11a[a]**

| Entry | Equiv AIBN | Yld **14a** | Yld **15a** |
|---|---|---|---|
| 1 | 0.25 | 73% | 12% |
| 2 | 0.50 | 71% | 15% |
| 3 | 0.75 | 76% | 10% |
| 4 | 1.0 | 77% | 8% |
| 5 | 2.0 | 71% | 9% |

**a) $C_6H_6$, 80°C, 0.01 M $Bu_3SnH$ (1.1 equiv relative to 11c).**

## Conclusion

In summary, the results with fragmentation probes **11a** and **11b** show the β-fragmentation reactions of α-acyloxy and α-alkoxycarbonyloxy radicals to give ketones and acyl or alkoxycarbonyl radicals (Figures 3,4) are, at best, slow reactions. Only traces of ketone **15** were detected in the reduction of **11b** even at very low concentrations, and a conservative upper limit for the fragmentation of this type of radical at 80°C is $<10^3$ $s^{-1}$. Small but variable amounts of ketone **15** (7–16%) were produced during cyclizations of **11b**, so the related α-acyloxy radical fragmentations to give acyl radicals could have rate constants as high as $10^3$ – $10^4$ $s^{-1}$. However, the results can also be interpreted through the intermediacy of cationic precursors of ketones produced by radical oxidation, in which case the rate constant for fragmentation is even smaller. Even if the β-fragmentation is occurring by a radical pathway, it is so slow as to have limited synthetic value in radical chain sequences. The sluggishness of these β-fragmentation reactions is surprising, especially give that they produce a strong C = O bond and a stable radical.

In the bigger picture, the results suggest that continued evaluation of the role of β-fragmentation reactions in self-terminating oxidative radical reactions is worthwhile. While the reaction conditions of our probe experiments and prior preparative experiments are very different, the slowness of the β-fragmentations to produce acyl and alkoxycarbonyl radicals suggests that such reactions may not be very competitive under any standard preparative conditions. If fragmentations do not occur to produce acyl and alkoxycarbonyl radicals with reasonable rate constants, then it is unlikely that fragmentations to produce unstable alkyl radicals (for example, $CH_3$•) or a hydrogen atom (H•) will occur. A similar conclusion has recently been reached through calculations by Sigmund, Wille, and Schiesser [17]. Either oxidative processes or group