Steric acceleration in the reaction of aryl bromides with tributylstannyl radicals

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Approximate absolute rate constants for the abstraction of bromine from a series of aryl bromides by stannyl radicals have been determined: 2,4,6-tri-*tert*-butylbromobenzene and 2,4,6-triphenylbromobenzene are found to be unusually reactive, most likely owing to steric acceleration.

Like many radical reactions,[1–5] the abstraction of a halogen atom from an aryl or vinyl halide by a stannyl radical is subject to polar effects. This much was demonstrated by Curran who showed that aryl halides carrying electron-withdrawing groups in the *ortho* or *para* positions react more rapidly with tin hydrides than do their unsubstituted congeners.[6] This is readily understood in terms of a polar transition state [eqn. (1)] with a partial negative charge on the sigma framework of the developing aryl radical.[6] We had therefore anticipated that 2,4,6-tri-*tert*-butylbromobenzene, with its sterically bulky, electron-donating alkyl groups, would be considerably less reactive than bromobenzene itself toward stannyl radicals. In the event, as we report here, the opposite was found to be the case: the abstraction of bromine from 2,4,6-tri-*tert*-butylbromobenzene by $Bu_3Sn\cdot$ is subject to a considerable acceleration due to the relief of steric strain.

In the course of an ongoing investigation, we had occasion to prepare 2,4,6-tri-*tert*-butyl- and 2,4,5-tri-iso-propylbromobenzene and to compare their reactivity toward tributyltin hydride with that of bromobenzene itself. Crude competition experiments revealed that, contrary to expectation, both were consumed somewhat more rapidly than the parent compound. We therefore undertook a more thorough investigation, comprising a series of competition experiments for a limited quantity of stannane. The initial and final ratios of both substrates in a given competition were determined by capillary GC or ^{1}H NMR spectroscopy, as appropriate, and the relative rates (k_{Rel}) computed using eqn. (2).[6,7]

$$k_1/k_2 = \{\ln[[\mathrm{Ar^1Br}]_i/([\mathrm{Ar^1Br}]_i - [\mathrm{Ar^1H}])]\}/\{\ln[[\mathrm{Ar^2Br}]_i/([\mathrm{Ar^2Br}]_i - [\mathrm{Ar^2H}])\} \qquad (2)$$

In this manner the relative rates set out in Table 1 were obtained.† The approximate absolute rate constants were then obtained using the known bimolecular rate constant for reaction of $Bu_3Sn\cdot$ with 1-bromodecane.[6] As is clear from Table 1, 2,4,6-tri-*tert*-butylbromobenzene is indeed considerably more reactive toward bromine abstraction by the stannyl radical than is 2,4,6-tri-iso-propylbromobenzene, being only slightly less reactive than 1-bromodecane. 2,4,6-Tri-iso-propylbromobenzene has comparable reactivity to 2-phenylbromobenzene and is some 2.6 times less reactive than 2-acetylbromobenzene. As this latter was found to be 6.7 times more reactive than 4-*tert*-butylbromobenzene, considered to be a model for bromobenzene itself, by Curran,[6] we conclude that 2,4,6-tri-iso-propylbromobenzene is some 2.6 times more reactive than bromobenzene. 2,4,6-Triphenylbromobenzene[8,9] was found to have identical reactivity to 1-bromodecane. We also studied pentafluorobromobenzene and found that it was so reactive toward the stannyl radical that we were unable to determine accurate ratios in competition experiments with 2-acetylbromobenzene; consequently we report a only minimum relative rate. With the likely exception of the perfluoroalkyl bromides,[10] pentafluorobromobenzene is the most reactive aryl or alkyl bromide toward stannyl radicals studied to date.

The reactivities of 2-phenyl- and 2-acetyl-bromobenzene are fully in accord with the polarized transition state [eqn. (1)] proposed by Curran. That of pentafluorobromobenzene likewise fits this model, although we cannot rule out an electron transfer chain mechanism in this case. The enhanced reactivity of 2,4,6-tri-iso-propylbromobenzene and especially that of 2,4,6-tri-*tert*-butylbromobenzene we attribute to acceleration due to relief of steric strain.‡ Such examples of steric acceleration of bimolecular radical reactions are much less common[1,11] than their unimolecular counterparts.[12] The reactivity of 2,4,6-triphenylbromobenzene can be ascribed to the symbiosis of three effects: (i) the stabilization of the polar transition state by the three phenyl groups phenyl substituents, (ii) relief of steric strain and (iii) relief of steric inhibition of resonance. However, as with pentafluorobromobenzene, we cannot rule out a single electron transfer mechanism in this case.

In conclusion, we have provided evidence that the abstraction of bromine from aryl bromides by stannyl radicals is accelerated when it leads to a relief of steric strain with bulky *ortho* substituents. Moreover, this acceleration is sufficient to overcome unfavourable polar effects in the transition state.

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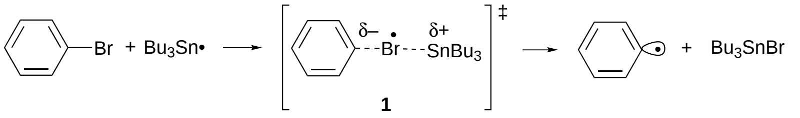
Table 1 Relative reactivity of aryl bromides toward tributyltin radicals

Entry	Bromide	k_{Rel}	$k/\mathrm{M}^{-1}\,\mathrm{s}^{-1}$
1	Pentafluorobromobenzene	>50	$>1 \times 10^8$
2	1-Bromodecane	15.2	5.8×10^7
3	2,4,6-Triphenylbromobenzene	15.2	5.8×10^7
4	2,4,6-Tri-*tert*-butylbromobenzene	9.5	2.9×10^7
5[a]	2-Acetylbromobenzene	6.7	1.6×10^7
6	2-Phenylbromobenzene	2.6	6.2×10^6
7	2,4,6-Tri-iso-propylbromobenzene	2.6	6.2×10^6
8[a]	4-*tert*-Butylbromobenzene	1	2.4×10^6

[a] Taken from ref. 6.



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Footnotes and References

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[†] All experiments were conducted a minimum of two times with good reproducibility.

[‡] Space filling molecular models (CHEM3D) show that while the bromine atom in both 2,4,6-tri-*tert*-butylbromobenzene and 2,4,6-triphenylbromobenzene is in a very congested environment, it is sufficiently well-exposed to permit abstraction by $Bu_3Sn\cdot$ through a linear transition state.

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