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Absolute Rate Constant for the Reaction of Aryl Radicals with Tri-*n*-butyltin Hydride[1]

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> *"A knowledge of the rates with which a radical R• is generated, rearranged and trapped by tin hydride now permits the rational planning of such free-radical reactions".*[4]

For over a quarter of a century an important activity at the National Research Council of Canada (NRCC) has been the measurement of the absolute rate constants for the reactions of carbon-centered radicals with tri-*n*-butyltin hydride.[5−8]

$$\mathrm{R}^\bullet + n\text{-}\mathrm{Bu_3SnH} \xrightarrow{k_\mathrm{H}} \mathrm{RH} + n\text{-}\mathrm{Bu_3Sn}^\bullet \qquad (1)$$

The availability of k_H values for a very wide variety of $\mathrm{R}^\bullet$ structures has undoubtedly contributed to the popularity of rational synthetic strategies which make use of free-radicals and tin hydride.[4,9−11] However, when we attempted to measure k_H for $\mathrm{R}^\bullet = \mathrm{C_6H_5}^\bullet$ by our (then) new laser flash photolysis (LFP) technique[7] we were misled by the view prevailing at that time that the photolysis of dibenzoyl peroxide gave phenyl radicals "instantaneously".[12] However, we later demonstrated[13−16]

$$(\mathrm{PhCO_2})_2 \xrightarrow{h\nu} 2\mathrm{Ph}^\bullet + 2\mathrm{CO_2} \qquad (2)$$

that the 308 nm LFP of diaroyl peroxides (including dibenzoyl peroxide[14]) gave aroyloxyl radicals which subsequently undergo a relatively slow decarboxylation. It

$$(\mathrm{ArCO_2})_2 \xrightarrow{h\nu} 2\ \mathrm{ArCO_2}^\bullet \qquad (3)$$

$$\mathrm{ArCO_2}^\bullet \xrightarrow{\text{slow}} \mathrm{Ar}^\bullet + \mathrm{CO_2} \qquad (4)$$

appeared, therefore, that the rate constant which we had measured in the dibenzoyl peroxide/tin hydride system, viz.,[7] $5.9 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$ at 30 °C, and had assigned to hydrogen atom abstraction by phenyl radicals, reaction 5, had to be reassigned to the benzoyloxyl radical/tin hydride reaction.

$$\mathrm{Ar}^\bullet + n\text{-}\mathrm{Bu_3SnH} \xrightarrow{k_\mathrm{H}} \mathrm{ArH} + n\text{-}\mathrm{Bu_3Sn}^\bullet \qquad (5)$$

We now describe the determination, by two independent methods, of k_H and also of k_D, the rate constant for deuterium abstraction from tri-*n*-butyltin deuteride by aryl radicals. One method is based on new LFP data for the reaction of aryl radicals with tetrahydrofuran (THF) and its perdeutero derivative (TDF) in aqueous solution. The other utilizes LFP data reported earlier by Scaiano and Stewart[12] for the reaction of phenyl radicals with methyl methacrylate in Freon 113. The two independent values which can be calculated for k_H ($\mathrm{R}^\bullet$ = aryl) are in reasonable agreement with one another. At last, therefore, it is possible to apply conventional competitive kinetic techniques to determine the magnitude of the rate constants for reactions of aryl radicals with other compounds of chemical[7,17] and biochemical[18] importance.

Results

Measurement of k_H and k_D by Intermolecular Competitions with TDF and THF. A major difficulty associated with kinetic studies on aryl radicals is their high reactivity toward all common organic solvents. We have recently demonstrated[21] that this problem can be overcome by 308 nm LFP of the sodium salt of 4-iodobenzoic acid (1.55×10^{-2} M)[22] in water. The kinetic behavior of the resultant aryl radical was monitored at 320 nm via its reaction with the water-soluble "probe"[23,24] molecule, the sodium salt of 4-styrenesulfonic acid, which was employed at a concentration of 2.0×10^{-3} M in the probe experiments. The global rate constants for reaction of this aryl radical with the probe,[24] k_probe, and with perdeuterotetrahydrofuran, tetrahydrofuran, and a few other compounds, k_gl, were measured in the usual way (incremental additions of the substrate at a constant concentration of the probe), i.e.,

$$k_\mathrm{exptl} = k_\mathrm{probe}[\mathrm{probe}] + k_\mathrm{gl}[\mathrm{substrate}] \qquad (\mathrm{I})$$

These rate constants are given in Table 1.

A radical chain reaction between iodobenzene and tri-*n*-butyltin deuteride (nominally 97 atom % D) at ca. 1:10 mole ratio was carried out in THF as solvent at 31 °C

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[24] In Scheme 1 this reaction is written as an addition to form a benzylic radical which is the species presumed to be mainly responsible for the grow-in of the 320 nm absorption. However, the global rate constant measured with this substrate includes all modes of reaction including, for example, addition to the aromatic ring.

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Table 1. Absolute Rate Constants for Reaction of the 4-$^-O_2CC_6H_4^•$ Radical with some Substrates in Water at 25 ± 2 °C

substrate	$k_{gl}/10^7\ M^{-1}\ s^{-1}$ [a]
$H_2C{=}CHC_6H_4SO_3^-$	$32._5 \pm 1.5_0$ (k_{probe})
THF[b]	$0.37_5 \pm 0.03_0$ (k_{THF})
TDF[c]	$0.13_2 \pm 0.00_3$ (k_{TDF})
2-cyclohexen-1-ol	$3.7_2 \pm 0.2_3$
$H_2C{=}CHC(CH_3)_2OH$	$2.9_6 \pm 0.1_6$
$HC{\equiv}CC(CH_3)_2OH$	$1.4_6 \pm 0.1_1$
furan	$2.3_5 \pm 0.3_1$

[a] Errors are expressed as 2σ (95% confidence limit) but include only random errors. Rate constants which are employed in the text are given in parentheses. [b] Tetrahydrofuran. [c] Perdeuterotetrahydrofuran.

(see Scheme 1). The chain reaction was initiated by photolysis of the deoxygenated mixture (see Experimental Section) in a Pyrex reaction vessel with light having $\lambda > 300$ nm. The iodobenzene was completely consumed within 15 min and at this time a sample of the reaction mixture was analyzed by GC/MS. The relative abundance of the ions at m/z = 76, 77, 78, 79, and 80 were determined by selective ion monitoring and the actual relative yields of benzene, $(C_6H_6)_{actual}$, and benzene-d_1 $(C_6H_5D)_{actual}$, (i.e., concentrations of benzene corrected for the contribution of the M-1 ion from benzene-d_1 and concentrations of benzene-d_1, corrected for contributions from natural abundance ^{13}C and ^2H in benzene) were calculated as described in the Experimental Section.

In order to obtain the true rate constant ratio, k_{THF}/k_D, two corrections must be applied. First, the nominal concentration of n-Bu_3SnD must be reduced by 4% to allow for the fact that the purity of this material was only 96.0%. The second correction arises from the fact that the n-Bu_3SnD was not 100% deuterated. The claimed isotopic purity was 96.6 atom % D which could imply as much as 3.4% n-Bu_3SnH which would serve as an "extra" source of C_6H_6. In addition, there was the possibility that some of the phenyl radicals which react with n-Bu_3SnD would abstract *hydrogen* from the butyl groups rather than deuterium from the SnD moiety thus giving additional "extra" C_6H_6. The correction for C_6H_6 formation in the $C_6H_5^•/n$-Bu_3SnD reaction was checked experimentally by photolysis (4 min, $\lambda > 300$ nm) of phenyl iodide in neat n-Bu_3SnD (ca. 1:10 mole ratio). In three separate experiments the mean actual yield of C_6H_6 was found to be 2.8 ± 0.5% of the total yield of benzene ($C_6H_5D + C_6H_6$) − which implies that there is little or no hydrogen abstraction from the butyl groups by the phenyl radical. The actual yield of C_6H_6 (calculated as described in the Experimental Section) must therefore be reduced by 2.8% before the true magnitude of the rate constant ratio, k_{THF}/k_D, can be determined. If all of these corrections are applied, we have:

$$\frac{k_{THF}}{k_D} = \frac{(C_6H_6)_{actual} - 0.028\,(C_6H_5D)_{actual}}{(C_6H_5D)_{actual}} \times \frac{(0.960 \times 0.972)\,(n\text{-}Bu_3SnD)_{nominal}}{[THF]} \qquad (II)$$

The results of five separate experiments and the values calculated for k_{THF}/k_D are summarized in Table 2.

In a second series of experiments the rate constant, k_{TDF}, for aryl radical attack on perdeuterotetrahydrofuran (TDF, > 99.5 atom % D) was measured by LFP (*vide supra*, Table 1 and Scheme 1). A radical chain reaction

Scheme 1

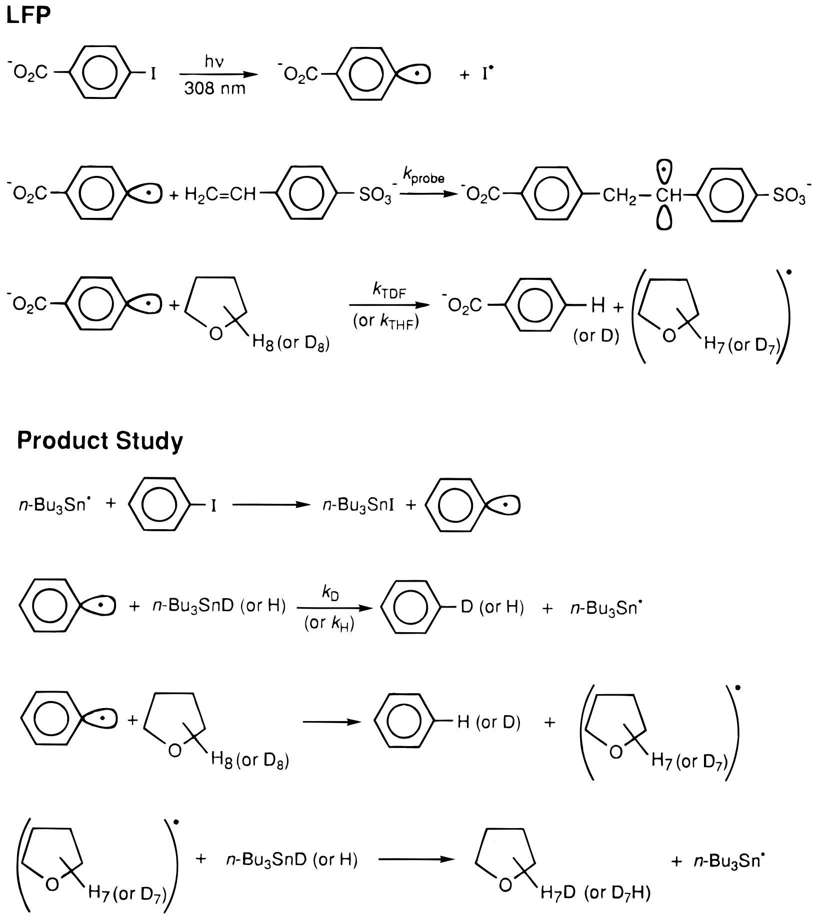

Table 2. Reaction of Iodobenzene with Tri-*n*-butyltin Deuteride in Tetrahydrofuran at 31 °C[a]

reactants (mol)					
$10^5 \times$ PhI	$10^4 \times$ n-Bu_3SnD[b]	$10^2 \times$ THF	THF/n-Bu_3SnD[b]	C_6H_6/C_6H_5D[c]	$10^2 \times k_{THF}/k_D$[d]
1.13	1.08	1.22	113	0.970	0.858
1.42	1.35	1.23	91.1	0.838	0.920
2.40	1.89	1.24	65.6	0.597	0.910
2.01	1.60	1.22	76.3	0.735	0.963
1.08	2.06	1.22	59.2	0.588	0.993

[a] Experiments are listed in the order in which they were carried out. [b] The moles of n-Bu_3SnD have been corrected for the purity and atom % in the following manner: $(n\text{-}Bu_3SnD)_{actual} = (n\text{-}Bu_3SnD)_{nominal} \times 0.960 \times 0.972$, where the n-Bu_3SnD was supplied as 96.0% purity and the atom % was determined from the mean values of three experiments where iodobenzene was photolyzed in neat n-Bu_3SnD. [c] This ratio was calculated from the ion intensities of $m/z = 78$ and 79 and solution of the two simultaneous equations as detailed in the Experimental Section. The intensity data for C_6H_6 has been corrected for C_6H_6 formation from the n-Bu_3SnH present in the n-Bu_3SnD sample: $(C_6H_6)_{actual} = (C_6H_6) - [0.028 \times 0.96 \times (C_6H_5D)]$. [d] $k_{THF}/k_D = (C_6H_6/C_6H_5D)^c/(THF/n\text{-}Bu_3SnD)^b$.

Table 3. Reaction of Iodobenzene with Tri-*n*-butyltin Hydride in Perdeuteriotetrahydrofuran at 31 °C[a]

reactants (mol)					
$10^5 \times$ PhI	$10^5 \times$ n-Bu_3SnH[b]	$10^2 \times$ TDF[c]	TDF/n-Bu_3SnH	C_6H_6/C_6H_5D[d]	$10^2 \times k_{TDF}/k_H$[e]
1.03	16.9	1.27	75.1	7.74	0.172
1.03	1.57	1.27	809	0.506	0.244
1.08	3.53	1.27	360	1.41	0.197
0.931	6.83	1.28	187	2.84	0.188
1.08	2.47	1.27	514	0.936	0.208

[a] Experiments are listed in the order in which they were carried out. [b] Since the n-Bu_3SnH was supplied as 97% purity, the moles of n-Bu_3SnH have been reduced by 3%. [c] The perdeuteriotetrahydrofuran (TDF) was supplied as 99.5+ atom % deuterium and hence no correction was applied for incompletely deuterated TDF. [d] This ratio was calculated from the ion intensities of $m/z = 78$ and 79 and solution of the two simultaneous equations as detailed in the Experimental Section. [e] $k_{TDF}/k_H = 1/\{(C_6H_6/C_6H_5D) \times (TDF/n\text{-}Bu_3SnH)\}$.

Table 4. Reaction of *p*-Iodotoluene (~0.5 M) with Tri-*n*-butyltin Hydride (Deuteride) and Methyl Methacrylate in Cyclohexane at 25 °C

$[n\text{-}Bu_3SnH]$[a] (M)	[MMA] (M)	[ArH][b]/[Add-H]	$[n\text{-}Bu_3SnD]$[a] (M)	[MMA] (M)	[ArD(H)][b]/[Add-D]
0.12	1.31	0.61	0.14	1.31	0.54
0.22	1.42	0.81	0.25	1.45	0.69
0.40	1.35	1.7	0.42	1.40	1.25
0.72	1.20	3.1	0.74	1.25	2.2

[a] Average concentration of n-Bu_3SnH or n-Bu_3SnD during the reaction. [b] Ratio of yields of toluene (ArH or ArD + ArH) to reduced first adduct (Add-H or Add-D) as measured by GC.

of iodobenzene and n-Bu_3SnH in TDF was carried out in the manner described above (see also Scheme 1). The results of these experiments are summarized in Table 3. In order to obtain the true rate constant ratio, k_{TDF}/k_H, where k_H refers only to abstraction of the hydrogen atom from tin, i.e., from the Sn*H* moiety, it would be necessary to correct the actual yield of C_6H_6 for C_6H_6 formed by hydrogen atom abstraction from the butyl groups of n-Bu_3SnH. Since this reaction is unimportant with n-Bu_3SnD we can safely ignore it with n-Bu_3SnH. Furthermore, since the TDF contained 99.5 + atom % D no correction is necessary for C_6H_6 formed in the $C_6H_5^{\bullet}$/TDF reaction. Since the n-Bu_3SnH was only 97% pure the equation used to derive the k_{TDF}/k_H ratios given in Table 3 was:

$$\frac{k_{TDF}}{k_H} = \frac{(C_6H_5D)_{actual}}{(C_6H_6)_{actual}} \times \frac{0.97(n\text{-}Bu_3SnH)_{nominal}}{[TDF]} \qquad \text{(III)}$$

Measurement of k_H and k_D by Intermolecular Competition with Methyl Methacrylate (MMA). The radical chain reduction of *p*-iodotoluene, ArI, with n-$Bu_3SnH(D)$ in the presence of MMA affords mixtures of toluene, ArH(D), and the adduct, $ArCH_2CH(Me)CO_2Me$ (Add-H) or $ArCH_2CD(Me)CO_2Me$ (Add-D):

$$n\text{-}Bu_3Sn^{\bullet} + ArI \rightarrow n\text{-}Bu_3SnI + Ar^{\bullet} \qquad (6)$$

$$Ar^{\bullet} + n\text{-}Bu_3SnH(D) \xrightarrow{k_{H(D)}} ArH(D) + n\text{-}Bu_3Sn^{\bullet} \qquad (5)$$

$$Ar^{\bullet} + CH_2{=}C(Me)CO_2Me \xrightarrow{k_{MMA}} ArCH_2\dot{C}(Me)CO_2Me\ (Add^{\bullet}) \qquad (7)$$

$$Add^{\bullet} + n\text{-}Bu_3SnH(D) \rightarrow Add\text{-}H(D) + n\text{-}Bu_3Sn^{\bullet} \qquad (8)$$

The relative rate of formation of ArH and Add-H is given by:

$$d[ArH]/d[Add\text{-}H] = (k_{SH}[SH] + k_H[n\text{-}Bu_3SnH])/k_{MMA}[MMA] \qquad \text{(IV)}$$

where k_{SH} represents the total H-atom donor ability of the reactant mixture.[25] Under pseudo-first-order conditions, i.e., low conversion of n-Bu_3SnH, this equation approximates to:

$$[MMA]([ArH]/[Add\text{-}H]) = k_{SH}[SH]/k_{MMA} + k_H[n\text{-}Bu_3SnH]/k_{MMA} \qquad \text{(V)}$$

Thus, a plot of [MMA]([ArH]/[Add-H]) against [n-Bu_3SnH] should give a straight line with a slope equal to k_H/k_{MMA}. For the reaction of ArI with n-Bu_3SnD the relevant equation is:

$$[MMA]([ArD]/[Add\text{-}D]) = k_{SH}[SH]/k_{MMA} + k_D[n\text{-}Bu_3SnD]/k_{MMA} \qquad \text{(VI)}$$

This equation applies because only the total yield of toluene was measured (by GC), not the actual yield of ArD (by, e.g., GC/MS), and because it seems safe to assume that the $Add^{\bullet}$ radical will react only with n-Bu_3SnD.

The experiments were conducted by adding n-$Bu_3SnH(D)$ and a catalytic amount of di-*tert*-butyl hyponitrite to a solution containing about 1 mol equiv of *p*-iodotoluene and an excess of MMA in cyclohexane. The reactions were stopped after 2 h by which time they had proceeded about 5−10% toward completion. The mixtures were then quenched by the addition of carbon tetrachloride and analyzed by GC.[26] Four experiments were carried out with n-Bu_3SnH and four with n-Bu_3SnD (see Table 4). Plots according to eqs V and VI yield $k_H/k_{MMA} = 5.0 \pm 0.6$ with $k_{SH}[SH]/k_{MMA} = 0.17 \pm 0.24$, and $k_D/k_{MMA} = 3.5$

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(25) The potential H-atom donors include MMA, the benzylic methyl group of *p*-iodotoluene and the cyclohexane solvent.

(26) Polymerization (i.e., $Add^{\bullet}$ + MMA→) and stannylation (i.e., n-$Bu_3Sn^{\bullet}$ + MMA→) afforded minor byproducts under our conditions (i.e., $[n\text{-}Bu_3SnH(D)]/[MMA] \geq 0.05$, $[ArI]/[MMA] \geq 0.3$).

± 0.4 with $k_{SH}[SH]/k_{MMA} = 0.21 \pm 0.16$, where the errors correspond to 2σ.

Discussion

Because the SOMO in aryl radicals lies in the plane of the aromatic ring, i.e., these are "isolated" σ-radicals,[27,28] substituents on the ring are expected (and have been shown)[29] to have only a relatively minor effect on the rates of reactions of these radicals.[30] We can therefore assume that the two aryl radicals generated in the present work, viz., $4\text{-}^{-}O_2CC_6H_4^{\bullet}$ and $4\text{-}CH_3C_6H_4^{\bullet}$, should have rather similar reactivities. For the reactions investigated, solvent effects are also expected to be relatively unimportant despite the wide range of solvents employed.[31] The small difference in the temperatures employed in the product studies (31 °C) and in the LFP measurements (25 ± 2 °C) can also be ignored.

The kinetic picture which emerges from the experiments involving intermolecular competition reactions with THF and TDF is (i) $k_{THF} = (3.75 \pm 0.30) \times 10^6$ M^{-1} s^{-1} (Table 1) and $k_{THF}/k_D = (0.929 \pm 0.093) \times 10^{-2}$ (Table 2), from which:

$$k_D = (4.04 \pm 0.73) \times 10^8\ M^{-1}\ s^{-1}$$

and (ii) $k_{TDF} = (1.32 \pm 0.03) \times 10^6$ M^{-1} s^{-1} (Table 1) and $k_{TDF}/k_H = (0.202 \pm 0.048) \times 10^{-2}$ (Table 3), from which:

$$k_H = (6.53 \pm 1.70) \times 10^8\ M^{-1}\ s^{-1}$$

where all errors have been expressed as 2σ but include only random errors. These data give a deuterium kinetic isotope effect, DKIE, $k_H/k_D = 1.6$, which is somewhat larger than previously reported values for aryl radicals, viz., 1.4[32] and 1.3.[33]

The kinetic picture which emerges from the intermolecular competition reactions with MMA is (iii) $k_{MMA} = 1.8 \times 10^8$ M^{-1} s^{-1} [12] and $k_D/k_{MMA} = 3.5 \pm 0.4$ (*vide supra* and Table 4) from which:

$$k_D = (6.3 \pm 0.7) \times 10^8\ M^{-1}\ s^{-1}$$

and (iv) $k_H/k_{MMA} = 5.0 \pm 0.6$ (*vide supra* and Table 4) from which:

$$k_H = (9.0 \pm 1.1) \times 10^8\ M^{-1}\ s^{-1}$$

and hence $k_H/k_D = 1.4$.

The k_D values derived from the THF experiments, viz., $(4.0 \pm 0.7) \times 10^8$ M^{-1} s^{-1}, and from the MMA experiments, viz., $(6.3 \pm 0.7) \times 10^8$ M^{-1} s^{-1} differ by slightly more than our 95% (random error) confidence limits. Hopefully, their mean value, viz., 5.2×10^8 M^{-1} s^{-1} will be fairly reliable.[34] More gratifyingly, the k_H values derived from the TDF experiments, viz., $(6.5 \pm 1.7) \times 10^8$ M^{-1} s^{-1}, and from the MMA experiments, viz., $(9.0 \pm 1.1) \times 10^8$ M^{-1} s^{-1}, are in agreement within our 95% confidence limits. Our recommended value for the rate constant for the reactions of aryl radicals with n-Bu$_3$SnH at ambient temperatures is the mean of the two measured values,[35] viz.,

$$k_H = 7.8 \times 10^8\ M^{-1}\ s^{-1}$$

At 80 °C (a temperature at which a great deal of synthetic chemistry is carried out with tin hydride) we estimate that $k_H \approx 1.0 \times 10^9$ M^{-1} s^{-1}.

Experimental Section

Materials. The following compounds were purchased from Aldrich and were generally used without further purification:

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(30) Except when the radical center is protected by two bulky ortho-substituents.[27]

(31) These two assumptions receive support from the agreement between the values of k_H/k_{MMA} and k_D/k_{MMA} calculated from the data in Table 4 via eqs V and VI, viz., 5.0 ± 0.6 and 3.5 ± 0.4, respectively (*vide infra*).

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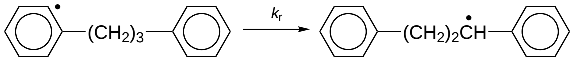
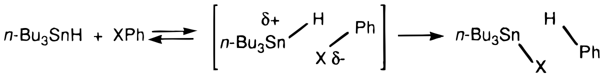
(34) In this connection, we note that some years ago we attempted to measure k_D using o-(3-phenylpropyl)iodobenzene as the source of an aryl radical which could rearrange by an intramolecular abstraction of a benzylic hydrogen atom (eq i). In isooctane at 25 °C an LFP study gave $k_{exptl} = (1.4 \pm 0.2) \times 10^7$ s^{-1} for the growth of the rearranged radical but this rate constant is not k_r since it also included contributions from any first- and pseudo-first-order processes which the radical undergoes, *including* H-atom abstraction from the solvent, rate constant, k_{OCT}. A photoinitiated radical chain reaction of this iodide with n-Bu$_3$SnD in isooctane at 25 °C followed by ^{2}H NMR analysis showed only an aromatic and a benzylic deuterium. From the ratio of these two products at known concentrations of n-Bu$_3$SnD we obtained $k_D/k_r = 35 \pm 4$ M^{-1}, and hence $k_D \leq 4.9 \times 10^8$ M^{-1} s^{-1} which implies that this ortho-substituted phenyl radical is somewhat less reactive than the $4\text{-}CH_3C_6H_4^{\bullet}$ and $4\text{-}^{-}O_2CC_6H_4^{\bullet}$ radicals. The rough magnitude of the correction to k_r for reaction with the solvent was determined by photolyzing PhI (0.02 M) and n-Bu$_3$SnD (0.1 M) in isooctane and analyzing for C_6H_6 and C_6H_5D. After applying all corrections we found that 4.8% of the benzene was due to phenyl radical attack on the isooctane. Thus, for the phenyl radical itself, $k_{OCT}[OCT] = 0.048\ k_D\ [n\text{-}Bu_3SnD] = 0.0048\ k_D = 4.8 \times 10^{-3} \times 5.2 \times 10^8 = 2.5 \times 10^6$ s^{-1}, and hence $k_{OCT} \approx 4 \times 10^5$ M^{-1} s^{-1}.



(1)

(35) Serious attempts were made to improve the accuracy of k_H by measuring k_H/k_D in direct competition experiments using n-Bu$_3$SnH/n-Bu$_3$SnD mixtures and iodobenzene or bromobenzene and analyzing for the C_6H_6/C_6H_5D ratios. To avoid complications due to H-atom abstraction from the solvent the reactions were photo-initiated using a deficiency of the halobenzene in mixtures of (neat) n-Bu$_3$SnH and (neat) n-Bu$_3$SnD (ca. 1:10:10 mole ratio). After applying all necessary corrections (see Experimental Section) we discovered to our surprise that the measured $k_H/k_D = 1.0$ (see Table 5 in the Supplementary Material for typical results with iodobenzene). This was demonstrated to be a "peculiarity" of the phenyl radical since using haloalkanes which would yield primary alkyl radicals we obtained k_H/k_D (1-pentyl) = 2.1 ± 0.1 by direct competition in neat n-Bu$_3$SnH/n-Bu$_3$SnD, and k_H/k_D (5-hexenyl) = 2.3 ± 0.1 by inter/intramolecular competition, both reactions being run in decane at 25 °C. The literature gives k_H/k_D (1-butyl) = 2.3 by LFP.[6] Our initial "explanation" for these results with the phenyl halides was that H(D)-atom abstraction by phenyl radicals in neat n-Bu$_3$SnH/n-Bu$_3$SnD was a diffusion-controlled process. Unfortunately, this simple "explanation" cannot be correct because the viscosity of neat n-Bu$_3$SnH is only 1.5 cP at 20 °C[36] and a diffusion-controlled radical-molecule reaction in a solvent of this viscosity would have a rate constant of about 4×10^9 M^{-1} s^{-1} [37] which is at least five times as large as our measured value for k_H. The reason for the peculiar behavior of phenyl radicals in neat n-Bu$_3$SnH/n-Bu$_3$SnD mixtures is not clear. However, we tentatively suggest that we were not irradiating the phenyl halide *per se*, but rather we were irradiating phenyl halide/tin hydride charge transfer complexes and that this process gave benzene and tin halide directly and immediately with no possibility of H/D discrimination by free phenyl radicals.



(36) We thank Witco GmbH, Bergkamen, Germany, for providing this data and an unknown referee for encouraging us to pursue the origin of the peculiarity of the neat n-Bu$_3$SnH/n-Bu$_3$SnD system.

(37) $(k_{diff}/M^{-1}\ s^{-1}) = 2 \times 10^7\ T/\eta$ with η in cP, see: Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publ. Co.: Menlo Park, California, 1978; p 314.

tri-*n*-butyltin hydride, (97% pure), tri-*n*-butyltin deuteride (96.0% pure, 96.6 atom % D), 4-iodobenzoic acid, 4-iodotoluene (colorless crystals, 99.8% pure by GC), sodium salt of 4-styrene sulfonic acid, tetrahydrofuran (THF purified by distillation from Na/K alloy), perdeuterotetrahydrofuran (99.5+ atom % D) and methyl methacrylate (MMA purified by distillation on a Dufton column, the 99.9−100.0 °C fraction was 99.8% pure by GC and was stored in a brown bottle at −20 °C).

Purification of Iodobenzene. Iodobenzene (10.0 g, Aldrich) in ether (20 mL) was treated with an aqueous solution of sodium thiosulfate (0.10 M, 30 mL). The ether solution was separated and passed through a column of basic alumina. The elution was completed using an additional quantity of ether (20 mL). The ether was removed at room temperature on a rotary evaporator, and the residue was fractionally distilled under reduced pressure. Pure, colorless iodobenzene was collected at 74 °C/15−20 Torr (8.9 g, 89% yield). It was stored in the dark over copper wire (which had previously been treated with a strong aqueous nitric acid solution, rinsed, and dried).

Laser Flash Photolysis (LFP). The general procedures have been adequately described in numerous other publications from this laboratory.[6−8,12−14,21]

Reaction of Iodobenzene with Tri-*n*-butyltin Deuteride in Tetrahydrofuran. A typical experiment was carried out as follows. Into a rubber septum-capped Pyrex tube were added, via syringe, iodobenzene (2.3 mg, 11.3 μmoles), tetrahydrofuran (THF, 1 mL, 0.880 g, 12.2 mmol) and *n*-Bu_3SnD (33.9 mg, 116 μmol). This mixture was cooled to −78 °C (acetone, dry ice) and purged with a slow, steady stream of nitrogen for 15 min. The reaction mixture was then warmed to room temperature and was photolyzed for 15 min in a Rayonet reactor (at 31 °C) with $\lambda > 300$ nm light. A sample of the reaction mixture (5 μL) was then immediately injected onto a Hewlett Packard HP-1 column of a GC/MS (Hewlett-Packard 5890 gas chromatograph combined with a 5970 series mass selective detector) and the relative abundance of the ion peaks at m/z = 76, 77, 78, 79, and 80 was determined by selective ion monitoring. Under these conditions all the iodobenzene was consumed.

The corrections to the apparent C_6H_6/C_6H_5D ratios (i.e., m/z 78/79 ratios) for natural abundance ^{13}C and ^2H and for the $(M - 1)^+$ peak were determined on the same GC/MS instrument using 5 μL aliquots of solutions of benzene (2.0 mg, 3.5 mg and 5.0 mg) in THF (1 mL). The intensities of the m/z = 77, 78, and 79 peaks were corrected for the background signal, this correction being based on a 2 min portion of the GC/MS spectrum devoid of any true signal. As a result of the three independent experiments with C_6H_6 the mean contributions to m/z = 78 and 79 are 93.55 ± 0.06% and 6.448 ± 0.056%, respectively, where the errors are 2σ. For C_6H_5D the corresponding figures for m/z = 78 and 79 are 24.60 ± 0.19% and 75.40 ± 0.19%, respectively.

The observed abundances of the peaks at m/z = 78 and 79 were proportioned into the contributions actually due to C_6H_6 and to C_6H_5D by solving the two following equations:

$$m/z\ (78)\text{intensity} = 93.55\ (C_6H_6)_{\text{actual}} + 24.60\ (C_6H_5D)_{\text{actual}}$$

$$m/z\ (79)\text{intensity} = 6.45\ (C_6H_6)_{\text{actual}} + 75.40\ (C_6H_5D)_{\text{actual}}$$

Although these two equations yield the $(C_6H_6)_{\text{actual}}/(C_6H_5D)_{\text{actual}}$ ratios there are two additional corrections which must be applied before the true rate constant ratio, k_{THF}/k_D, can be calculated. The first involves correcting the nominal quantity of *n*-Bu_3SnD used in each experiment for the fact that this material was only 96.0% pure. The second arises from potential sources of C_6H_6 in the $C_6H_5^\bullet$/*n*-Bu_3SnD reaction. There are two potential sources of C_6H_6 in this reaction: (i) a *n*-Bu_3SnH impurity, (ii) hydrogen abstraction from the butyl groups of *n*-Bu_3SnD by the $C_6H_5^\bullet$ radical. With regard to (i) the claimed isotopic purity was 96.6 atom % deuterium which could imply as much as 3.4% *n*-Bu_3SnH as an impurity. To check on the real relative yield of C_6H_6 in the $C_6H_5^\bullet$/*n*-Bu_3SnD reaction a solution of phenyl iodide in *n*-Bu_3SnD (ca. 1:10 mole ratio) was photolyzed (4 min, $\lambda > 300$ nm). Product analysis showed that $(C_6H_6)_{\text{actual}} = 0.028\ [(C_6H_5D)_{\text{actual}} + (C_6H_6)_{\text{actual}}]$ which probably means that there is about 2.8% *n*-Bu_3SnH present in the *n*-Bu_3SnD (rather than 3.4%). Thus,

$$\begin{aligned}(n\text{-}Bu_3SnD)_{\text{actual}} &= 0.960 \times 0.972\ (n\text{-}Bu_3SnD)_{\text{nominal}} \\ &= 0.933\ (n\text{-}Bu_3SnD)_{\text{nominal}}\end{aligned}$$

Furthermore, because 2.8% of "extra" C_6H_6 is formed in the $C_6H_5^\bullet$/*n*-Bu_3SnD reaction, the actual yield of C_6H_6 must be corrected in order to obtain the quantity of C_6H_6 formed by phenyl radical abstraction from THF:

$$(C_6H_6)_{\text{THF}} = (C_6H_6)_{\text{actual}} - 0.028\ (C_6H_5D)_{\text{actual}}$$

We have employed the above corrections to calculate the k_{THF}/k_D ratios given in Table 2. That is,

$$\frac{k_{\text{THF}}}{k_D} = \frac{(C_6H_6)_{\text{actual}} - 0.028\ (C_6H_5D)_{\text{actual}}}{(C_6H_5D)_{\text{actual}}} \times \frac{0.933\ (n\text{-}Bu_3SnD)_{\text{nominal}}}{[\text{THF}]}$$

Reaction of Iodobenzene with Tri-*n*-butyltin Hydride in Perdeuterotetrahydrofuran. Experiments were conducted in an identical manner to those employed to study the *n*-Bu_3SnD/THF competition. Since the TDF contained 99.5 + atom % D no correction was considered to be necessary for C_6H_6 formed in the $C_6H_5^\bullet$/TDF reaction. Furthermore, because the C_6H_6 formed in the $C_6H_5^\bullet$/*n*-Bu_3SnD reaction appears to come entirely from a *n*-Bu_3SnH impurity (*vide supra*) no correction would appear to be necessary for C_6H_6 formed by $C_6H_5^\bullet$ abstraction from the butyl groups of *n*-Bu_3SnX (X = H, D, I). Thus, the only correction required is to the quantity of *n*-Bu_3SnH employed because this material was only 97% pure:

$$\frac{k_{\text{TDF}}}{k_H} = \frac{(C_6H_5D)_{\text{actual}}}{(C_6H_6)_{\text{actual}}} \times \frac{0.97(n\text{-}Bu_3SnH)_{\text{nominal}}}{[\text{TDF}]}$$

This equation was used to derive the final column in Table 3.

Reaction of *p*-Iodotoluene with Tri-*n*-butyltin Hydride (Deuteride) and Methyl Methacrylate in Cyclohexane. In a typical experiment, *n*-$Bu_3SnH(D)$ (50 μL, 185 μmol) and di-*tert*-butyl hyponitrite (0.6 mg, 4 μmol) were added to a solution of *p*-iodotoluene (∼40 mg, ∼200 μmol) and MMA (50 μL, 425 μmol) in cyclohexane (200 μL). The mixture was then freeze-pump-thaw degassed and flame-sealed i*n vacuo* in an 800 μl Carey tube. After standing for ∼2 h at ambient temperature, the ampoule was opened and the contents were added to 400 μL of argon-purged CCl_4. The solution was warmed to 43 °C for 0.5 h and then analyzed by capillary GC (Varian 6500 instruments/25 m BP1 column) using the pure addends for reference.[38] The mean concentration of *n*-$Bu_3SnH(D)$ (92− 95% of the initial value) was calculated from the ratio *n*-Bu_3Snl/*n*-Bu_3SnCl (GC) in the quenched mixture. The results are tabulated in Table 4.

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Supporting Information Available: Table 5 with product data for the reaction of iodobenzene with (neat) *n*-Bu_3SnH/(neat) *n*-Bu_3SnD mixtures (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[38] Bordwell, F. G.; Carlson, M. W. *J. Am. Chem. Soc.* **1970**, *92*, 3370−3377.