pound **8i** could not be isolated in a pure state but its presence could safely be inferred by the presence of a doublet at δ 1.70 (Me, $J_{4,\mathrm{Me}}$ = 7.9 Hz) and of a ddd at δ 3.07 (H-5, J = 2.0, 7.0, and 8.5 Hz), in the ^{1}H NMR spectrum ($CDCl_3$) of the **7i** + **8i** mixture.

7l: slightly brown oil with a higher R_f than **8l** (cyclohexane/AcOEt, 9:1, as eluant); IR 1540 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.98 (d, Me, $J_{4,\mathrm{Me}}$ = 7.0 Hz), 0.90–1.90 (m, 8 H), 2.45 (m, H-7), 4.38 (m, H-4, $J_{1,4} = J_{4,5}$ = 2.5 Hz), 4.48 (ddd, H-1, $J_{1,5}$ = 6.0 Hz and $J_{1,7}$ = 2.5 Hz). $\Delta\delta$ 0.24 (Me), 0.17 (H-7), 0.27 (H-4), 0.27 (H-1). **8l**: slightly brown oil; IR 1540 cm^{-1}; ^{1}H NMR (C_6D_6) 1.36 (d, Me, $J_{4,\mathrm{Me}}$ = 7.0 Hz), 0.88–1.80 (m, 7 H), 2.10 (m, H-6), 2.42 (m, H-7), 4.15 (m, H-4, $J_{4,5}$ = 7.5 Hz and $J_{1,4} \leq$ 1.0 Hz), 4.30 (dd, H-1, $J_{1,5}$ = 6.0 Hz and $J_{1,7}$ = 2.0 Hz). $\Delta\delta$ 0.26 (Me), 0.42 (H-6), 0.10 (H-7), 0.37 (H-4), 0.34 (H-1).

9a: colorless needles from cyclohexane; mp 60–63 °C; IR 1740, 1540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.02 (s, OAc), 2.10 (s, OAc), 2.84 (m, H-5), 5.38 (ddd, H-6, $J_{5,6} = J_{6,7}$ = 6.9 Hz and $J_{1,6}$ = 2.4 Hz), 5.62 (ddd, H-7, $J_{1,7}$ = 6.9 Hz and $J_{5,7}$ = 2.4 Hz), 5.65 (m, H-1), 5.98 (dd, H-4, $J_{1,4} = J_{4,5}$ = 2.7 Hz). $\Delta\delta$ 0.38 (OAc), 0.46 (OAc), 0.66 (H-5), 0.38 (H-6), 0.27 (H-7), 0.40 (H-1), 0.03 (H-4). Anal. Calcd for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.59; N, 9.72. Found: C, 62.35; H, 5.65; N, 9.85.

9e: colorless needles from benzene; mp 115–116 °C dec (lit.[7b] mp 116–117 °C); IR 1540 cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.02 (m, H-5), 4.04 (ddd, H-6, $J_{5,6} = J_{6,7}$ = 7.5 Hz, and $J_{1,6}$ = 2.1 Hz), 4.24 (ddd, H-7, $J_{1,7}$ = 7.3 Hz and $J_{5,7}$ = 2.5 Hz), 4.90 (m, H-1), 6.15 (dd, H-4, $J_{1,4} \simeq J_{4,5}$ = 2.8 Hz). $\Delta\delta$ 0.93 (H-5), 0.91 (H-6), 0.88 (H-7), 0.86 (H-1), 0.10 (H-4). Anal. Calcd for $C_{11}H_{10}Cl_2N_2$: C, 54.77; H, 4.15; N, 11.61. Found: C, 54.90; H, 4.18; N, 11.81. We were able to isolate a higher R_f product ($\simeq$3%), but its fast decomposition to give a reddish product has made it impossible, to date, to characterize it.

9f: colorless platelets from methanol: mp 120–122 °C; IR 1733, 1538 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.96 (m, H-5) 2.84 (dd, H-6, $J_{5,6} = J_{6,7}$ = 9.5 Hz), 3.24 (s, OMe), 3.36 (s, OMe), 3.56 (ddd, H-7, $J_{1,7}$ = 9.0 Hz and $J_{5,7}$ = 2.5 Hz), 5.02 (ddd, H-1, $J_{1,5}$ = 7.2 Hz and $J_{1,4}$ = 2.6 Hz), 6.60 (dd, *H*-4, $J_{4,5}$ = 5.0 Hz). $\Delta\delta$ 0.60 (H-5), 0.79 (H-6), 0.43 (OMe), 0.35 (OMe), 0.51 (H-7), 0.68 (H-1), −0.33 (H-4). Anal. Calcd for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.59; N, 9.72. Found: C, 62.33; H, 5.59; N, 9.73. **10f** and **11f** were isolated as a mixture (slightly yellow oil). The ^{1}H NMR spectrum of this mixture displayed four singlets at δ (C_6D_6) 3.20 and 3.35 (methoxy groups in **11f**) and at δ 3.42 and 3.46 (methoxy groups in **10f**) thus clearly disclosing the presence of two adducts: IR 1738, 1535 cm^{-1}. Anal. Found: C, 62.60; H, 5.45; N, 9.65.

9i: colorless needles from benzene; mp 133–135 °C dec; IR 1800, 1540 cm^{-1}. Anal. Calcd for $C_{12}H_{10}N_2O_3$: C, 62.60; H, 4.38; N, 12.17. Found: C, 62.66; H, 4.38; N, 12.14. Adducts **10i** and **11i** were obtained as a mixture from column chromatography and separated by fractional crystallization. **10i**: colorless leaflets from benzene; mp 166–168 °C dec; IR 1800, 1540 cm^{-1}. Anal. Found: C, 62.70; H, 4.50; N, 12.10. **11i**: colorless prisms from chloroform; mp 140–142 °C dec; IR 1800, 1540 cm^{-1}. Anal. Found: C, 62.76; H, 4.24; N, 12.22.

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Registry No. **1a**, 71348-58-8; **1b**, 126036-72-4; **1c**, 67520-63-2; **1d**, 126036-73-5; **1e**, 2957-95-1; **1f**, 42577-15-1; **1g′**, 126036-74-6; **1g″**, 126108-41-6; **1h**, 126036-75-7; **1i**, 33186-71-9; **1j**, 115977-19-0; **1k**, 61253-93-8; **1l**, 4927-03-1; **1m**, 616-10-4; **2a**, 101219-81-2; **2b**, 126036-76-8; **2c**, 121399-69-7; **2d**, 126036-77-9; **2e**, 121829-49-0; **2f**, 121399-74-4; **2g′**, 126036-78-0; **2g″**, 126108-42-7; **2h**, 126036-79-1; **2m**, 126036-81-5; **3e**, 126108-21-2; **3f**, 121468-35-7; **3g′**, 126108-27-8; **3g″**, 126108-43-8; **3h**, 126108-28-9; **3m**, 126108-29-0; **4a**, 113749-60-3; **4b**, 126036-82-6; **4c**, 121399-72-2; **4d**, 126036-83-7; **4e**, 19877-63-5; **4g′**, 126109-24-8; **4h**, 126036-84-8; **4i**, 113749-65-8; **5a**, 113829-20-2; **5b**, 126108-30-3; **5c**, 121468-34-6; **5d**, 126108-31-4; **5e**, 19877-62-4; **5f**, 22160-73-2; **5g′**, 126036-85-9; **5g″**, 126108-44-9; **5h**, 126108-32-5; **5i**, 113829-26-8; **5j**, 126036-86-0; **5l**, 113749-71-6; **6a**, 126108-22-3; **6e**, 121829-50-3; **6f**, 126036-87-1; **6i**, 126108-33-6; **7e**, 126108-23-4; **7f**, 126108-34-7; **7i**, 126108-35-8; **7l**, 126108-36-9; **8e**, 126108-24-5; **8f**, 126108-37-0; **8i**, 126108-38-1; **8l**, 126108-39-2; **9a**, 126036-70-2; **9e**, 121829-53-6; **9f**, 126108-40-5; **9i**, 126187-26-6; **10f**, 126036-80-4; **10i**, 126036-71-3; **11f**, 126108-26-7; **11i**, 126108-25-6; *cis*-3,4-dihydroxycyclobutene, 60090-87-1; benzyl chloride, 100-44-7; diazomethane, 334-88-3; 2-diazopropane, 2684-60-8; diazoethane, 1117-96-0; phenyldiazomethane, 766-91-6.

On the Mechanism of the Radical Chain Transformation of Nitroalkanes to Alkanes Using Triaryl- or Trialkyltin Hydrides[1]

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The standard potentials, $E°$, for the oxidations and reductions of triphenyl- and tributylstannyl radicals in THF containing 0.1 M tetrabutylammonium perchlorate (TBAP) have been estimated by a combination of electrochemical and kinetic measurements. Lower limits of $E°$ for the oxidations are >−0.42 V and >−0.43 V (vs SCE) respectively for the triphenylstannyl radical and the tributylstannyl radical. The oxidation potentials of the stannyl radicals were combined with the reduction potentials of nitroalkanes to define the thermochemistry for the electron-transfer reaction between these species. It was found that the electron-transfer reaction was not a feasible propagation step in the reactions of stannyl radicals with simple nitroalkanes and that an addition/elimination sequence must apply.

Nitroalkanes can be converted to their corresponding alkanes by using tributyltin hydride[2,3] or nicotinamide derivatives[4] as reducing agents. Initially,[2,3a] the tin hydride reaction mechanism was thought to invoke an electron transfer between the stannyl radical and the nitroalkane as one of the propagation steps, eqs 1–3. However, an

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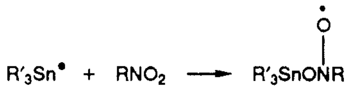
$$RNO_2^{\bullet-} \rightarrow R^\bullet + NO_2^- \quad (1)$$

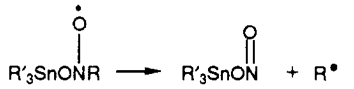
$$R^\bullet + R'_3SnH \rightarrow RH + R'_3Sn^\bullet \quad (2)$$

$$R'_3Sn^\bullet + RNO_2 \rightarrow R'_3Sn^+ + RNO_2^{\bullet-} \quad (3)$$

alternative mechanism was subsequently suggested[5] in which the tin radical adds to the nitro compound to give a nitroxyl radical that, in turn, fragments to yield the chain-propagating alkyl radical, eqs 4 and 5. Although



$$R'_3Sn^\bullet + RNO_2 \longrightarrow R'_3SnO\overset{\overset{\bullet}{O}\,|}{N}R \quad (4)$$



$$R'_3SnO\overset{\overset{\bullet}{O}\,|}{N}R \longrightarrow R'_3SnO\overset{O\,\|}{N} + R^\bullet \quad (5)$$

the alternative mechanism is plausible, the experimental justification for its proposal is less than convincing.

Spectroscopic studies of the reactive intermediates shed little light on which of these mechanistic possibilities was correct. Electron paramagnetic resonance (EPR) studies of such reductions gave spectra that were attributed to nitroalkane radical anions with proximate tin cations as the counter ions, I.[6] However, it was subsequently rec-

$$RNO_2^\bullet MBu_3^+$$

I

$$R\overset{\overset{\bullet}{O}\,|}{N}OMBu_3$$

II

M = Si, Ge, Sn, Pb

ognized[7] that radicals with essentially identical spectral parameters have been assigned to nitroxides, II.[8-10] In fact, the EPR parameters themselves are equally consistent with both possibilities and do not provide a means of discriminating between them.

To differentiate between the electron-transfer versus the addition–elimination mechanisms, we have taken a different approach and have attempted to measure the requisite redox potentials of the nitroalkanes and of the trialkyl- and triaryltin radicals. These data define the thermochemistry for the electron-transfer process and hence provide an insight into its viability. In addition, we measured rate constants for the reaction between trialkylstannyl radicals and nitroalkanes by using laser flash photolysis techniques. We anticipated that these results could be used to resolve the question of the reaction mechanism.

Results and Discussion

Reduction Potentials of Nitroalkanes. Cyclic voltammograms of nitrocyclohexane (III), 2-methyl-2-nitropropane, and α-nitrocumene were obtained at room temperature in tetrahydrofuran (THF) and acetonitrile at glassy carbon and platinum microelectrodes. Scan rates of 20 V/s to 1000 V/s revealed quasireversible reductions for all of the compounds. Estimates of the $E_{1/2}$ values were obtained by averaging the positions of the anodic and cathodic peaks and the values are reported in Table I (these averages were independent of scan rate). Relatively large peak separations of 400 to 600 mV were observed in THF, consistent with the recent report by Bowyer and Evans on the reduction of III at Hg microelectrodes in dimethylformamide (DMF).[11] Peak separations in acetonitrile were typically about 100 to 400 mV. The $E_{1/2}$ values are notably different in the two solvents and are also quite different from the values reported in DMF,[11] indicating that solvation and liquid junction effects make comparison between solvents difficult.

Table I. Cyclic Voltammetry of Nitroalkanes in THF and Acetonitrile[a]

compound	solvent	scan rate (V/s)	$E_{1/2}$ (V vs SCE)
CumylNO$_2$	THF	500	−1.14
$C_6H_{11}NO_2$		1000	−1.00
t-BuNO$_2$		50	−1.21
CumylNO$_2$	acetonitrile	20	−0.89
$C_6H_{11}NO_2$		20	−0.88
t-BuNO$_2$		20	−0.85

[a] At a platinum microelectrode (10 μm diameter) using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte.

The results cited above demonstrate that the reduction potentials of simple nitroalkanes are solvent dependent but are relatively insensitive to the structure of the alkyl group. We therefore only required the oxidation potentials of stannyl radicals to define the thermochemistry for the electron-transfer process (reaction 3). However, our attempts to make these measurements by using conventional and photomodulation voltammetry were thwarted by experimental difficulties (vide infra).

Voltammetric Measurements on Tricoordinate Tin. Several studies of the electrochemistry of triaryltin cations have been reported,[12-14] but the results remain equivocal. We initially examined the polarographic reduction of solutions of Ph_3Sn^+ using Dessy's method,[12] eqs 6 and 7, in which the cation was prepared by the addition of 95% of the stoichiometric amount of $AgClO_4$ to Ph_3SnCl or Ph_6Sn_2 in THF containing 0.1 M tetrabutylammonium perchlorate (TBAP). However, we found that both the triphenyltin cation and the hexaphenylditin reacted directly with mercury, giving a black precipitate. Polarographic analysis was therefore unreliable, vitiating earlier studies,[12,13] and voltammetric analysis on solid electrodes was used instead.

$$AgClO_4 + Ph_3SnCl \rightarrow Ph_3Sn^+ClO_4^- + AgCl \quad (6)$$

$$2AgClO_4 + Ph_6Sn_2 \rightarrow 2Ph_3Sn^+ClO_4^- + 2Ag^0 \quad (7)$$

The voltammetry of the tin cations was studied by using gold, platinum, and glassy carbon electrodes. The results were complex and were dependent not only on the sweep rate but also on the history of the electrode. For example, a continuously cycled gold microelectrode (10 μm diameter) gave a reduction wave on the negative sweep at −0.9 V and an oxidation wave that varied between 0.12 and 0.36 V versus SCE. The peak that appeared in the range 0.12 to 0.36 V showed a current dependence that was linear with respect to the sweep rate, indicating that the peak was due

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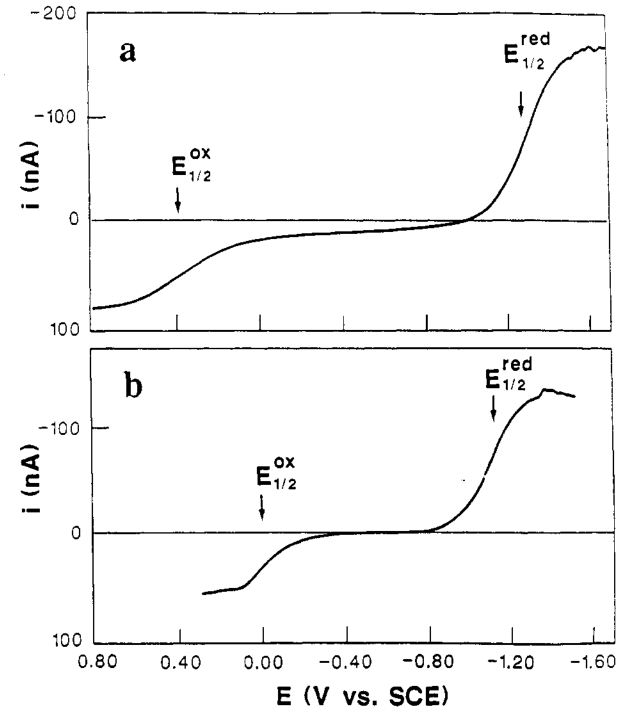

Figure 1. Voltammogram obtained by using the PMV technique from the photolysis of a solution of (a) Bu_6Sn_2 in THF (0.1 M TBAP) and (b) di-*tert*-butyl peroxide (0.5 M) containing Bu_3SnH (0.01 M) in acetonitrile (0.1 M TBAP).

to a species present on the gold surface. In fact, it was shown that a surface film had been formed since the cycled electrode, when rinsed (but not repolished) and transferred to a fresh solution of THF and electrolyte, gave several oxidation and reduction peaks. Qualitatively similar results were obtained for the voltammetry at the other electrode surfaces. Overall the results indicated that surface films were corrupting the measurements of the redox potentials.

Photomodulation Voltammetry (PMV).[15] Modulated photolysis, through a gold minigrid electrode, of a solution of hexaphenylditin, eq 8, in THF containing 0.1 M TBAP with phase-sensitive electrochemical detection gave a voltammogram with a reduction wave at −0.59 V (vs SCE) and a much smaller oxidation wave at 0.12 V on the initial scan. Subsequent scans led to a progressive anodic shift of the oxidation wave to 0.60 V. However, no shift in the reduction wave was observed. These results were similar to those obtained by cyclic voltammetry on the gold microelectrode (vide supra). We demonstrated that some modification of the gold surface had occurred by measuring a voltammogram of the diphenylmethyl radical[15] immediately after the experiment on the triphenyltin radical. The oxidation potential of $Ph_2CH^\bullet$ was shifted anodically by 100 mV and the reduction potential was shifted cathodically by 150 mV.

$$Ph_3Sn_2 \xrightarrow{h\nu} 2Ph_3Sn^\bullet \qquad (8)$$

A similar experiment using hexabutylditin in THF/0.1 M TBAP, eq 9, gave a voltammogram with a reduction wave at −1.29 V and an oxidation wave at 0.38 V (Figure 1a). These waves did not shift in subsequent scans. In acetonitrile/di-*tert*-butyl peroxide (9:1) containing 0.1 M TBAP and using tributyltin hydride as the source of the tin radical, eq 10 and 11, a reduction wave at −1.13 V and an oxidation wave at 0.00 V were observed (Figure 1b). The positions of these waves in both solvents were independent of the number of scans. In light of the surface modification of the electrode that occurred with the triphenyltin systems, we felt that it would be improper to place a great deal of confidence in the measured potentials for the tributylstannyl radical.

$$Bu_6Sn_2 \xrightarrow{h\nu} 2Bu_3Sn^\bullet \qquad (9)$$

$$t\text{-BuOOBu-}t \xrightarrow{h\nu} 2t\text{-BuO}^\bullet \qquad (10)$$

$$t\text{-BuO}^\bullet + Bu_3SnH \xrightarrow{\text{fast}} t\text{-BuOH} + Bu_3Sn^\bullet \qquad (11)$$

Table II. Electron-Transfer Reactions of $R_3Sn^{\bullet+}$

oxidant	reductant ($E°$)[a]	k_{obx} ($M\ s^{-1}$)[b]	$E°$ ($R_3Sn^+/R_3Sn^\bullet$) (V vs SCE)[c]
Bu_3Sn^+	Fe (0.50)	n.r.	
	DiMFe (0.36)	n.r.	
	DMP (0.31)	0.027	>−0.38
	TMPD (0.12)	3.36	>−0.44
	DMFe (0.10)	2.92	>−0.47
Ph_3Sn^+	Fe (0.50)	n.r.	
	DiMFe (0.36)	n.r.	
	DMP (0.31)	0.86	>−0.28
	TMPD (0.12)	7.32	>−0.42
	DMFe (0.10)	19.0	>−0.42

[a] Values versus SCE, measured in THF vs $Ag/AgClO_4$ (10^{-3} M), Pt electrode, 200 mV s^{-1}. [b] Measured in THF by stopped-flow spectrophotometry. n.r. = no reaction observed. [c] *Lower limit* estimated using eq 14.

Homogeneous Electron-Transfer Reactions of Trivalent Tin Cations. Since direct electrochemistry on solutions of the R_3Sn cation or radical was complicated by the formation of surface films, we attempted to estimate $E°(R_3Sn^+/R_3Sn^\bullet)$ from the rates of outer-sphere electron transfer.

Triphenyl- or tributyltin cation (0.005 M), prepared by the reaction of a deficiency of $AgClO_4$ with the corresponding tin chloride in THF as solvent, was allowed to react with equimolar amounts of suitable donors, D, in a stopped-flow absorption spectrometer. The donors chosen were ferrocene (Fe, $E° = 0.50$ V), dimethylferrocene (DiMFe, $E° = 0.36$ V), dimethylphenazine (DMP, $E° = 0.31$ V), *N,N,N′,N′*-tetramethylphenylenediamine (TMPD, $E° = 0.12$ V), and decamethylferrocene (DMFe, $E° = 0.10$ V). The growth of the absorptions due to the respective cations fitted second-order kinetics for at least 46% reaction to give the values of k_{obs} shown in Table II.

The overall mechanism for these electron-transfer processes can be written as a slow forward electron transfer after which the fate of $R_3Sn^\bullet$ is determined by the competition between the reverse electron-transfer reaction and diffusion-controlled, second-order self-reaction (eqs 12 and 13).

$$R_3Sn^+ + D \rightleftharpoons R_3Sn^\bullet + D^{\bullet+} \qquad (12)$$

$$2R_3Sn^\bullet \rightarrow R_6Sn_2 \qquad (13)$$

If the rate of reaction 13 is much greater than that for reverse electron transfer, then $k_{obs} = k_{12}$. However, if the rates are similar, then k_{obs} will represent a lower limit for k_{12}.[17]

In principle, $E°$ ($R_3Sn^\bullet/R_3Sn^+$) can be estimated from kinetic data by applying the Marcus equation.[18] However,

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Table III. Rate Constants for the Reaction of $R_3Sn^\bullet$ with Nitroalkanes[a]

compound	$10^{-8}k$ (M^{-1} s^{-1})
CH_3NO_2	0.73
$(CH_3)_2CHNO_2$	0.95
$(CH_3)_3CNO_2$	0.93
III	0.90

[a] Measured by laser flash photolysis in benzene.

the value of the reorganization energy, λ, is required for the calculation. Since this parameter has not been defined for the $R_3Sn^\bullet/R_3Sn^+$ couple in THF, Marcus theory cannot be quantitatively applied in this instance. Nevertheless, it is possible to define a lower limit for $E°(R_3Sn^\bullet/R_3Sn^+)$ using kinetic data in combination with eq 14, where $E°(D/D^+)$ represents the oxidation potential of the electron donor used in reaction 11.

$$\ln K_{eq} = \ln (k_{12}/k_{-12}) = F[E°(R_3Sn^\bullet/R_3Sn^+) - E°(D/D^+)]/RT \quad (14)$$

Since $k_{obs} \lesssim k_{12}$ and since k_{-12} cannot be greater than the diffusion-controlled limit, i.e., $k_{-12} \lesssim$ ca. 10^{10} M^{-1} s^{-1}, we can say that $K_{eq} \gtrsim 10^{-10}k_{obs}$ and we can therefore calculate lower limits for $E°(R_3Sn^\bullet/R_3Sn^+)$ using eq 14 and the values of $E°(D/D^+)$ cited above. The lower limits for $E°(R_3Sn^\bullet/R_3Sn^+)$ are reported in Table II.

Thermochemistry for the Reactions of Stannyl Radicals with Nitroalkanes. It is possible to calculate limiting values for the thermochemistry of reaction 3. If it is assumed that if reaction 3 proceeds by an outer-sphere electron-transfer mechanism, the change in free energy for the reaction is equal to $23.03[E°(R_3Sn^\bullet/R_3Sn^+) - E°(RNO_2^{\bullet-}/RNO_2)]$ kcal mol^{-1}. Combination of the data for simple nitroalkane reductions (Table I) with the limiting value for the oxidation potential of the tributylstannyl radical (Table II) implies that reaction 3 is a least 12 kcal mol^{-1} endoergonic. The data also indicate that the reactions which involve triphenylstannyl will be similarly endoergonic.

We now have to address the question of whether the thermochemistry for the electron-transfer mechanism is consistent with the rate constant for the reaction between stannyl radicals and nitroalkanes.

Laser Flash Photolysis Experiments. The laser flash photolysis technique was used to measure rate constants for the reactions of the tributylstannyl radical with several nitroalkanes. Tributylstannyl radicals were generated by photolysis of mixtures containing di-*tert*-butyl peroxide (25% v/v) and tributyltin hydride (0.3 M) in benzene as solvent, eqs 15 and 16. They were monitored at 400 nm

$$t\text{-BuOOBu-}t \xrightarrow{h\nu} 2t\text{-BuO}^\bullet \quad (15)$$

$$t\text{-BuO}^\bullet + Bu_3SnH \rightarrow t\text{-BuOH} + Bu_0Sn^\bullet \quad (16)$$

and the observed pseudo-first-order rate constants for their decay, k', were measured as a function of nitroalkane concentration,[19] reaction 17. The data were plotted according to eq 18, where k_0 was the lifetime of the stannyl radical in the absence of nitroalkane, and gave excellent

$$Bu_3Sn^\bullet + RNO_2 \rightarrow \text{products} \quad (17)$$

$$k' = k_0 + k_{17}[RNO_2] \quad (18)$$

straight lines from which the values of k_{17} were obtained. These values are reported in Table III.

Attempts were made to measure values of k_{17} in THF as solvent. However, attack by *tert*-butoxyl radicals at the solvent diminished the yield of stannyl radicals, reaction 16, to the point where their absorptions could no longer be monitored. However, if the electron-transfer mechanism were operative, the observed rate constant (as measured by laser flash photolysis) would almost certainly be greater in THF than in benzene. Thus, the data reported in Table III represent lower limits for k_{17} in THF.

The data obtained demonstrate that the reactions between stannyl radicals and nitroalkanes, eq 17, proceed with rate constants that are close to the diffusion-controlled limit (Table III). These results are quite inconsistent with the electron-transfer mechanism, reaction 3, which was demonstrated to be endoergonic by at least 12 kcal mol^{-1}. We therefore conclude that the simple addition mechanism, reaction 4, best describes the reactions since it is consistent with all of the available spectroscopic, kinetic, and electrochemical data.

Experimental Section

Materials. Reagent dimethylformamide (Aldrich, HPLC grade) was used as received. Solvent benzene was purified by the standard procedure.[20] The purification of α,α'-azobis(isobutyronitrile), *p*-di-*tert*-butylbenzene (internal standard), *m*-dinitrobenzene (DNB), and 1-benzyl-1,4-dihydronicotinamide (BNAH) have been described previously.[21] Tributyltin hydride (Aldrich) was used as supplied.

Commercial tetrahydrofuran (G.I.C.) was purified by allowing it to stand 15 days over potassium hydroxide and overnight over naphthalene/sodium and it was then distilled.

Hexaphenylditin, triphenyltin chloride tributyltin chloride, tetrabutylammonium perchlorate, and silver perchlorate were dried over P_2O_5 under vacuum at 60 °C. Ferrocene, dimethylferrocene, decamethylferrocene, and *N,N,N',N'*-tetramethylphenylenediamine were commercially available and were used as received. Dimethylphenazine was synthesized according to a literature procedure.[22]

Cyclic Voltammetry. Electrochemistry was performed on a Princeton Applied Research EG & G Model 175 Universal Programmer wave form generator equipped with an Amel Model 551 potentiostat that provided feedback compensation for ohmic drop between the working and reference electrodes. Voltammograms were recorded on a Princeton Applied Research Model RE0074 X–Y recorder for scan rates (γ) of 500 mV/s or less and a Tektronix 2430 digital oscilloscope equipped with a Hewlett-Packard Thinkjet printer when the scan rate was >500 mV/s. Electrochemical measurements were carried out at 25 °C in anhydrous THF solutions containing 5×10^{-3} M triphenyltin chloride, 97% of the stoichiometric amount of $AgClO_4$, and 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. The values are reported versus SCE and were measured in THF versus $Ag/AgClO_4$ (10^{-3} M). The carbon and gold electrodes were cleaned between each scan with a fine polishing powder on a soft cloth.

Photomodulation Voltammetry (PMV). The instrument has been described in detail elsewhere.[15] Briefly, the radicals were generated in the electrochemical cell by photolysis, through an optically transparent gold electrode, of a solution of R_6Sn_2 (ca. 0.05 M) in THF containing 0.1 M TBAP. The output from the lamp was modulated with a light chopper so the light intensity (and therefore the radical concentration) rose and fell as a sine wave. The electrochemical cell was fully *iR* compensated and was controlled by using a PAR Model 174A polarographic analyzer. The ac component of the Faradaic current was detected with an

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(19) Because the photolysis initiated the chain reduction of the nitroalkane, a different tube for each concentration of RNO_2 was used (5 laser shots max per tube).

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Ithaco Model 391A lock-in amplifier. A plot of the ac current as a function of the potential gave a voltammogram of the photogenerated free radical. All measurements were made at 53-Hz modulation with quadrature detection of the signal. The measured potentials are reported with respect to the saturated calomel electrode (SCE).

Kinetics. The triorganotin perchlorate was made by mixing the appropriate triorganotin chloride with an equivalent amount of silver perchlorate in THF. The silver chloride was removed by filtration and a fresh solution of cation perchlorate was used for the kinetic runs. An aliquot of solutions of R_3Sn^+ (5×10^{-3} M or 10^{-3} M) and DMFe (5×10^{-3} M) or TMPD (5×10^{-3} M) was transferred by syringe to the two compartments of a stop-flow apparatus (Hi-Tech Scientific Limited).

As a general procedure the decrease in the concentration of DMFe or TMPD was monitored by observing the appearance of DMFe$^{\cdot+}$ ($\epsilon = 21$) or TMPD$^{\cdot+}$ ($\epsilon = 425$) at 570 or 700 nm, respectively. The extinction coefficient of each radical-cation was determined by measuring the absorbance of a solution of the reaction mixture resultant from the reaction of DMFe or TMPD with a 97 mol % solution of $AgClO_4$. The metallic silver formed from the reaction was separated by centrifugation. The UV spectrometer used was a Unicam SP 1800.

Several control experiments were carried out in order to ensure that the generation of the ferrocenium ions was not due to residual levels of Ag^+ or of R_3SnCl. It was found that the tin chlorides did not react with TMPD or DMFe. However, the possibility remained that a detectable amount of Ag^+, due to the finite solubility of AgCl in THF, was responsible for the formation of the ferrocenium ions. This concern was eliminated by addition of ferrocene (0.001 M), which does *not* react with R_3Sn^+ but reacts readily with Ag^+. Aliquots of this "silver-free" solution of the tin cation were used to observe the oxidation reaction with TMPD, DMP, and DMFe.

Laser Flash Photolysis. The laser flash photolysis technique has been described in detail elsewhere.[23] Briefly, samples were irradiated with pulses from a nitrogen laser (337.1 nm, 8 ns duration, up to 10 mJ power) and the transients thus generated were monitored on a detection system consisting of a low powered xenon lamp and a monochromator fitted with a photomultiplier tube detector. Signals from the photomultiplier were digitized (Tektronix 7912) and were then transferred to a PDP 11/23 computer for storage and analysis.

In a typical experiment, a solution of Bu_3SnH (0.3 M) in a mixture of benzene/di-*tert*-butyl peroxide (4:1) were deoxygenated by nitrogen purging for 5 min. The decay of the $Bu_3Sn^\bullet$ radical was monitored (400 nm) as a function of the concentration of a nitro compound. A plot of k_{obs} versus concentration gave a straight line with the slope being the absolute rate constant.

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The Mechanism of Oxygen Transfer from an Oxaziridine to a Sulfide and a Sulfoxide: A Theoretical Study

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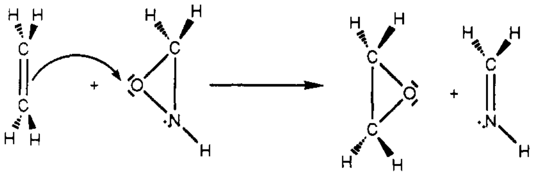
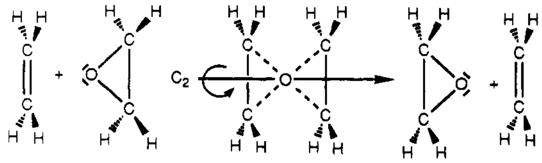
Chiral oxaziridines provide synthetically useful reagents for the asymmetric transfer of an oxygen atom to a variety of substrates. One of the fundamental questions pertaining to the approach of the reactants is whether either of the lone pairs on the electrophilic oxygen exerts a significant electronic influence on the transition structure. Employing a model reaction system, we have found that oxygen atom transfer from an oxaziridine to a sulfoxide is essentially invarient to the torsional orientation of the two fragments in the transition state. The planar and spiro transition structures differ in energy by only 0.4 kcal/mol at the MP4SDTQ/4-31G(d) level of calculation. These data are consistent with experimental observations and with the earlier ab initio calculations on this type of oxygen atom transfer.

Introduction

Oxygen transfer to a nucleophilic addend typically involves the cleavage of a relatively weak oxygen–oxygen or metal–oxygen σ-bond.[1] However, it has recently been shown[2] that a properly substituted oxaziridine functional group is a unique oxidizing agent in that a nucleophilic S_N2 type attack on the oxaziridine oxygen results in the displacement of an imine with transfer of its oxygen atom (eq 1). For example, in an alkene expoxidation reaction oxygen transfer to the nucleophilic carbon–carbon double bond is facilitated by the relatively weak oxygen–nitrogen bond and by the enthalpy of carbon–nitrogen π-bond



(equation 1)



(equation 2)

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