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KINETICS AND MECHANISM OF MERCURIDESTANNYLATION OF PHENYLSTANNATRANES AND RELATED DERIVATIVES

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Summary

The kinetics and mechanism of mercuridestannylation of phenylstannatrane derivatives, $PhSn(OCH_2CH_2)_3N$ and $PhSn(OC_6H_4)_3N$ have been investigated relative to model systems $PhSnBu_3$, $PhSn(OMe)_3$ in solvent MeOH. For the latter two, the reaction proceeded via the following pattern with $k_2 > 10\ k'_2$

$$R_3SnPh + HgI_2 \xrightarrow{k_2} R_3SnI + PhHgI \qquad \text{(i)}$$

$$R_3SnI + HgI_2 \overset{K}{\rightleftarrows} R_3Sn^+ + HgI_3^- \qquad \text{(ii)}$$

$$R_3Sn^+ + HgI_3^- + R_3SnPh \xrightarrow{k'_2} 2R_3SnI + PhHgI \qquad \text{(iii)}$$

For the stannatranes, step (iii) was not observed. The order of reactivity was shown to be $PhSnBu_3 > PhSn(OCH_2CH_2)_3N = PhSn(OC_6H_4)_3N \gg PhSn(OMe)_3$.

Arguments are made for rate-determining C–Sn bond fission in reaction (i). Stabilisation of the developing the charge on Sn is important and the enhanced reactivity of the stannatranes is explained by Sn–N transannular interactions.

Values of k_2 and k'_2 were obtained for $PhSnBu_3$ and $PhSn(OMe)_3$ which enabled K to be evaluated in each case.

Introduction

Since their discovery by Davies [1] in 1972, alkyl and arylstannatranes have been the subject of detailed structural analysis mainly with a view to establishing the existance of Sn–N intramolecular bonding *.

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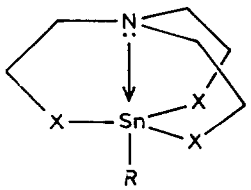
* IUPAC nomenclature designates these compounds as [2,2′,2″-nitrilotris(ethanolato)(3 –)-*N,O,O′,O″*]-tin derivatives.



(I)

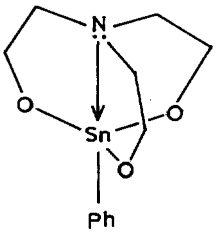
(X = O, CH_2)

Amongst the structural probes used, ^{119}Sn Mössbauer and ^{119}Sn NMR spectroscopies were anticipated to shed most light on the problem. Unfortunately, the former has the disadvantage that various values of isomer shifts (*IS*) and quadrupole splittings (*QS*) have appeared. Thus the original values [1] obtained for phenylstannatrane were *IS* 0.43, *QS* 1.18 mm s^{-1}. These were quickly followed by values of 0.94 (*IS*) and 1.66 mm s^{-1} (*QS*). This discrepancy has a very large effect on the *QS*/*IS* ratio which has been used to determine the coordination number of tin [3]. More recently [4], the method of partial *QS* has been used to show that pentacoordinacy does not occur for simple stannatranes in the solid phase. The results were more in keeping with hexacoordinates structures, which is in agreement with the observed self association of stannatranes in non-polar solvents [5,6] as evaluated from ^{15}N and ^{119}Sn NMR. The high field shifts of the Sn resonances and the appearance of $^{15}N-^{119}Sn$ coupling strongly indicates intramolecular N–Sn interactions. Very recently [7] a new stannatrane (I, $X = CH_2$, $R = Me$) has been reported with a $\delta(^{119}Sn)$ of -14.4 ppm which also implies N–Sn bonding, though even relatively small changes in C–Sn–C bond angles can cause large shifts [8] in the ^{119}Sn resonance. Further evidence comes from the observed slow rates of quaternisation of stannatranes with MeI [9]. We have undertaken a kinetic study of mercuridestannylation reaction on the rates and mechanisms of Sn–C bond fission in phenylstannatranes to evaluate the role of N–Sn interactions on reactivity.

Results and discussion

Relatively few kinetic studies have been made of metallotrane derivatives. Apart from the quaternisation reactions already mentioned [9], the only other detailed investigations have dealt with solvolysis reactions of silatranes [10–12] in which it was concluded that the rate-determining step involved protonation at nitrogen with concerted Si–N bond fission.

Our interest in mechanism of carbon–metal bond fission [13,14] led us to examine the mercuridestannylation reactions of the following stannatranes using $PhSnBu_3$ and $PhSn(OMe)_2$ as references. III has not previously been reported.



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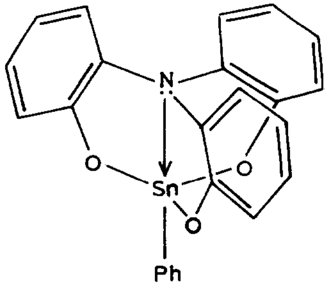


(III)

Mercuridestannylation

This reaction has been found to involve several steps [15,16]:

$$\mathrm{RSnR'_3 + HgX_2 \xrightarrow{k_2} RHgX + XSnR'_3} \tag{1}$$

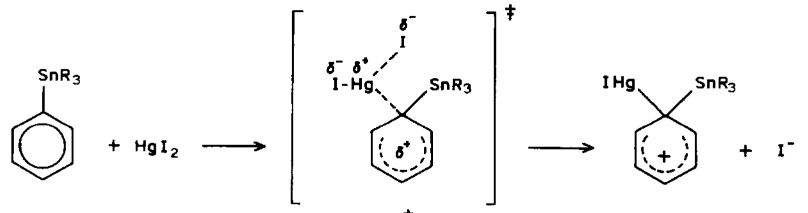
$$\mathrm{XSnR'_3 + HgX_2 \overset{K}{\rightleftarrows} [R'_3Sn^+][HgX_3^-]} \tag{2}$$

$$\mathrm{[R'_3Sn^+][HgX_3^-] + RSnR'_3 \xrightarrow{k'_2} RHgX + 2XSnR'_3} \tag{3}$$

Step (3) is usually very slow and (1) and (2) can generally be treated completely separately. Provided K is large, the kinetic equations employed are of a very simple nature [15]. The $PhSnR_3$ derivatives were treated with HgI_2 in MeOH and the reaction followed by monitoring the appearance HgI_3^- spectrophotometrically (λ 257, 325 nm). Formation of HgI_3^- reached a maximum at 50% reaction after which a slow decay via (3) occurred for the reference compounds $PhSnBu_3$ and $PhSn(OMe)_3$. Well defined isosbestic points were observed for the initial portion of this reaction. Process 3 either did not occur or was extremely slow for II and III. This suggests that the complex $[R'_3Sn^+][HgX_3^-]$ is more stable for the stannatranes compared with $PhSn(OMe)_3$. Both have the ability to stabilise the positive charge on tin via neighbouring oxygen atoms, but only the stannatranes have the possibility of extra stabilisation by the transannular nitrogen. In all cases Ph–Sn rather than Sn–O or $Sn{-}CH_2$ cleavage was observed. The kinetic results appear in Tables 1 and 2. From this data the order of reactivity is $PhSnBu_3 > II = III \gg PhSn(OMe)_3$. II and III show striking similarities over a wide temperature range. In all cases the reactions are simple second order processes whose rates are defined by

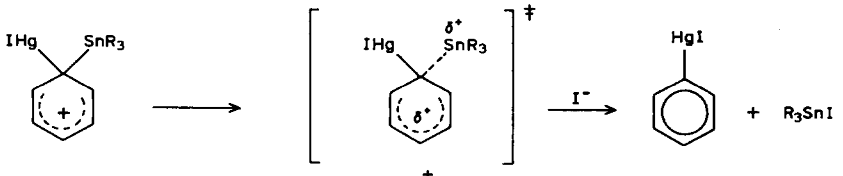
$$\mathrm{rate} = k_2[\mathrm{PhSnR_3}][\mathrm{HgI_2}] \tag{4}$$

Association of the stannatranes [5] is very unlikely in solvent methanol particularly at the concentrations used (1–5×10^{-4} M) in this work and the quite strict adherence of the data to eq. 4 supports this. Both II and III react considerably faster than $PhSn(OMe)_3$. The activation parameters listed in Table 3 show that the major difference in reactivity of II and $PhSn(OMe)_3$ lies in the $\Delta H^{\neq}$ rather than $\Delta S^{\neq}$ terms (the latter all have quite large negative values typical of a bimolecular process). Since the reaction is a typical electrophilic aromatic substitution, the question arises as to which step (5 or 6) is rate-determining.



(5‡)

(5)



(6‡)

(6)

TABLE 1

SECOND ORDER RATE CONSTANTS k_2 (M^{-1} s^{-1}) FOR THE CLEAVAGE OF $PhSnBu_3$, $PhSn(OMe)_3$, $PhSn(OCH_2CH_2)_3N$ AND $PhSn(OC_6H_4)_3N$ BY HgI_2 IN MeOH

$10^4[PhSnR_3]$ (M)	$10^4[HgI_2]$ (M)	k_2
$PhSnBu_3$ (23.7°C)		
1.00	1.00	10.2
1.25	1.25	10.8
1.50	1.50	10.1
2.00	2.00	10.7
2.50	2.50	10.8
2.00	1.00	10.5
2.50	1.00	10.3
1.00	2.50	10.7
1.00	2.00	10.8
$PhSn(OMe)_3$ (20.0°C)		
3.00	2.50	0.23
3.75	2.50	0.23
5.00	2.50	0.24
6.25	2.50	0.23
7.50	2.50	0.24
$PhSn(OCH_2CH_2)_3N$ (25.0°C)		
0.80	0.80	2.77
1.00	1.00	2.74
1.50	1.50	2.75
2.00	2.00	2.73
2.50	2.50	2.78
5.00	2.50	2.74
1.00	2.00	2.72
$PhSn(OC_6H_4)_3N$ (25.0°C)		
0.80	0.80	2.72
1.00	1.00	2.48
1.50	1.50	2.67
2.00	2.00	2.64
2.50	2.50	2.41
1.00	2.00	2.83
2.50	1.00	2.88

One important factor governing the relative stabilities of the two transition states (TS) is the strength of metal–carbon bonding, which in turn depends on whether the TS is "late" or "early". The relative bond strengths for C–Sn and C–Hg are about 60 and 32 kcal mol^{-1} [17] which suggests that the second step (eq. 6) is rate-determining, provided the TS is late. The same answer results from consideration of carbon–metal hyperconjugation [18]. In a nucleophilic solvent such as methanol, assistance by iodide ion is unlikely [19] and thus the developing charge on tin in step (6) will be stabilised by MeOH. Such solvation effects would be more sterically inhibited in $6^{\neq}$ than $5^{\neq}$ which would also increase the activation energy of the second step.

TABLE 2

VARIATION OF k_2 (M^{-1} s^{-1}) WITH TEMPERATURE (°C) FOR THE CLEAVAGE OF $PhSnR_3$ BY HgI_2 IN MeOH

$PhSnBu_3$	T	14.5	20.2	23.7	30.1	35.0	40.0	45.1
	k_2	6.4	8.8	10.4	14.5	17.7	23.2	28.4
$PhSn(OMe)_3$	T	20.0	25.0	30.0	35.0	45.0		
	k_2	0.23	0.40	0.48	0.75	1.23		
$PhSn(OCH_2CH_2)_3N$	T	15.0	20.0	25.0	30.1	35.0	40.0	45.0
	k_2	1.48	2.33	2.76	4.02	5.95	6.60	10.1
$PhSn(OC_6H_4)_3N$	T	20.0	25.0	30.0	35.0	40.0	45.0	
	k_2	2.36	2.64	3.89	5.50	6.40	10.1	

The chief difficulty in interpreting the kinetic data lies in the absence of any reliable assessment of the electronic effects stannatrane and $Sn(OMe)_3$ groups. Eaborn [20] has calculated a σ^+ value for the silatrane group of -0.24 which makes it more electron releasing than $SiMe_3$ and comparable with a methyl group. Voronkov [21,22] has used ^{13}C NMR to evaluate σ_I, for silatrane and related groups. Values of -0.40, -0.08 and $+0.01$ were obtained for the 1-silatranyl group, $Si(OEt)_3$ and $Si(OMe)_3$ respectively. Using the extensive ^{13}C data in Ewings review [23] and Exner's values of σ_R° [24] (taking for the sake of internal consistency only those values obtained from ^{19}F NMR) we have found an excellent correlation of Δ vs. σ_R°, $r = 0.981$ for a total of 62 points. This leads to the empirical relationship

$$\Delta = S_p - S_m = 20.77\sigma_R^\circ + 0.308 \qquad (7)$$

where S_p, S_m are the ^{13}C shifts for *para* and *meta* carbons, respectively, in C_6H_5X derivatives

From this, σ_R° values for the silatrane and $Si(OEt)_3$ groups are $+0.01$ and $+0.10$ respectively. This indicates that the resonance effect involves $p_\pi - d_\pi$ back-bonding to the silicon which is somewhat reduced by the intramolecular Si–N interaction. Unfortunately, phenylstannatrane is not soluble enough in the usual NMR solvents for ^{13}C data to be obtained, but it is unlikely that the σ_R° value will be very different. The HgI group probably behaves as $-I$ group with a weak $+M$ contribution resulting in overall electron withdrawal as opposed to overall electron

TABLE 3

ACTIVATION PARAMETERS ($\Delta H^{\neq}$, $\Delta G^{\neq}$ kcal mol^{-1}; $\Delta S^{\neq}$ cal K^{-1} mol^{-1}) FOR CLEAVAGE OF $PhSnR_3$ COMPOUNDS BY HgI_2 IN MeOH

Compound	$\Delta H^{\neq}$	$\Delta S^{\neq}$ [a]	$\Delta G^{\neq}$
$PhSnBu_3$	6.0±0.4	−29.1±1.3	13.9±0.6
$PhSn(OCH_2CH_2)_3N$	7.0±0.4	−28.4±1.3	14.8±0.6
$PhSn(OC_6H_4)_3N$	8.0±0.4	−25.4±1.9	14.9±0.6
$PhSn(OMe)_3$	10.0±0.5	−22.9±1.6	16.2±0.6

[a] Calcd. at 298 K.

TABLE 4

VARIATION OF k'_2 (M^{-1} s^{-1}) WITH TEMPERATURE FOR THE REACTION OF $PhSnR_3$ WITH $[R_3Sn^+][HgI_3^-]$ IN MeOH WITH CORRESPONDING ACTIVATION PARAMETERS ($\Delta H^{\neq}$ (kcal mol^{-1}), $\Delta S^{\neq}$ (cal K^{-1} mol^{-1}))

						$\Delta H^{\neq}$	$\Delta S^{\neq\ a}$
	$T = 20.2$	23.7	30.1	35.0	40.0		
R = n-Bu	$k'_2 =$ 0.70	0.90	1.52	1.89	2.78	12.0	−18.3
R = OMe	$T = 20.0$	25.0	30.0	35.0	45.0	10.6	−25.1
	$k'_2 =$ 0.23	0.36	0.39	0.68	1.05		

[a] Calcd. at 25°C.

release by the 1-stannatranyl group. This again suggests that $5^{\neq}$ will be more stable than $6^{\neq}$ and that step 6 is, therefore, rate-determining. It is thus possible to explain the observed relative rates in terms of stabilisation of the developing positive charge on tin in $6^{\neq}$. This can be achieved via Sn–N transannular interaction in the stannatranes which results in 11-fold rate increases relative to $PhSn(OMe)_3$. $PhSnBu_3$ has the highest rate due to electron release by the alkyl groups.

The third step of the reaction (eq. 3) could be followed conveniently only in the cases of $PhSnBu_3$ and $PhSn(OMe)_3$. The kinetic data for the reaction $[R_3Sn^+][HgI_3^-]$ appear in Table 4. Reaction 3 comprises two steps

$$[R_3Sn^+][HgI_3^-] \overset{K_{diss}}{\rightleftarrows} R_3SnI + HgI_2 \tag{8}$$

$$R_3SnPh + HgI_2 \rightarrow R_3SnI + PhHgI \tag{9}$$

The overall free energy ($\Delta G^{\neq}_{overall}$) of the process is given by

$$\Delta G^{\neq}_{overall} = \Delta G_{diss} + \Delta G^{\neq} \tag{10}$$

where ΔG_{diss} is the free energy of dissociation of the complex and $\Delta G^{\neq}$ is the activation energy already obtained from initial rate data. ΔG_{diss} can thus be evaluated. For Bu_3SnPh a value of 3.6 kcal mol^{-1} is obtained whereas for $(MeO)_3SnPh$ a lower figure is calculated of 1.9 kcal mol^{-1}. The free energies of association are thus −3.6 and −1.9 kcal mol^{-1}, respectively which leads to values of the association constants K of 440 and 25 respectively. These values reflect the greater ease with which iodide is lost from Bu_3SnI compared with $(MeO)_3SnI$.

Experimental

Methanol was of AnalaR quality, and was dried by refluxing over magnesium methoxide for 2 h, followed by distillation. The dried solvent was subsequently fractionated under nitrogen. Mercury(II) iodide was recrystallised twice from methanol and dried at 65°C/4 mmHg for several hours. MP 256-7 Phenylstannatrane was prepared in 83% yield from $PhSn(NEt_2)_3$ and triethanolamine in dry benzene (1.5 h). The product was recrystallised from $CHCl_3$ and was identical to that obtained by Zeldin and Ochs [9].

Phenyl(2,2′,2″-nitrilotriphenoxy)stannane (nc)

2,2′,2″-Nitrilotriphenol [25], (o-$C_6H_4OH)_3N$, (1.5 g, 5×10^{-3} mol) was dissolved in 20 ml of sodium-dried benzene and placed in a three-necked round-bottom flask, equipped with a funnel, magnetic stirring bar, condenser, Argon purge and $CaCl_2$ tubes. Phenyltris(dimethylamino)stannane (1.9 g, 5 mmol) in 10 ml of dry benzene was added dropwise from the funnel, with rapid stirring. A slight exotherm was detected and the reaction solution quickly became cloudy. After the addition was complete, the whole was left stirring for 30 min. The precipitate was filtered under argon, and recrystallised from chloroform. The product was an amorphous, white powder and was dried in a drying-pistol at 80°C/30 mmHg, for several hours. Yield was 2.1 g, 89%. M.p. > 350°C. The ^1H NMR spectrum (in $CDCl_3$ solution) showed the presence only of a series of complex aromatic multiplets, in the region 8.0–6.6 ppm. Molecular weight (ebulliometric in methanol); found, 500, calculated, 486. Analysis: Found: C, 58.8; H, 3.9; N, 3.4. $C_{24}H_{17}NO_3Sn$ calcd.: C, 59.3; H, 3.5; N, 2.9%.

$PhSn(OMe)_3$ [26]

This compound was prepared in situ without isolation of the solid. All operations involving it were carried out in a glove-box bag under a dry argon atmosphere.

Freshly distilled phenyltris(dimethylamino)stannane (0.60 ml, 0.444 g, 1.18×10^{-3} mol) was added dropwise via a syringe through a rubber septum to 40 ml of pure dry methanol. This resulted in vigorous fuming over the surface of the methanol. After the addition was complete, the system was evacuated to a pressure of 10 mmHg to remove the bulk of the dimethylamine formed during the reaction. The reaction flask was then frozen down in liquid nitrogen, and allowed to slowly warm up, whilst reducing the pressure to 0.1 mmHg. This freeze-pump-thaw cycle was repeated several times in order to ensure complete removal of the dimethylamine. An aliquot subsequently removed had no detectable odour of amine. The solution of phenyltrimethoxystannane thus prepared was then standardised by titration. Several 1.0 ml aliquots were mixed with 2.0 ml aliquots of standardised iodine solution, and left to stand overnight at 50°C. The iodine remaining was subsequently determined by titration with standard sodium thiosulphate solution under acid conditions, using starch solution to indicate the end-point. The results of the titrations were reproducible to $\pm 1\%$.

Product analyses

(i) TLC. A solution of phenyl stannatrane and mercury(II) iodide was made up to 1.00 ml (5.0×10^{-3} *M* in each) in methanol, and allowed to stand at 25.0°C) for several hours. Analysis of the reaction mixture using TLC was then carried out. The solution was spotted on Silica Gel GF_{254} (Merck) and eluted with chloroform. The plates were examined under UV, with iodine vapour and also by spraying with a 0.5% solution of dithizone (diphenylthiocarbazone, DTZ). Four spots [R_F values in parentheses] were identified as phenylstannatrane (0.0) mercury(II) iodide (0.54) and phenylmercuric iodide (0.74), respectively. The spot with $R_f = 0.36$ was assumed to be iodostannatrane. With the DTZ spray, these gave yellow, yellow-pink and yellow-orange spots, respectively. The spots were identified by comparison of R_f values with those of authentic samples which were eluted on the same plate as the reaction mixture.

TABLE 5

QUANTITATIVE PRODUCT ANALYSES FOR MERCURIDESTANNYLATION REACTIONS

Compound	Found (%) [a]	
	HgI_2 [b]	PhHgI [c]
$PhSnBu^n_3$	16	85
$PhSn(OCH_2CH_2)_3N$	47	53
$PhSn(OC_6H_4)_3N$	46	54
$PhSn(OMe)_3$	33	66

[a] Average of 4 determinations, except compound $PhSnBu^n_3$, average of 6 determinations. [b] Determined as $Cu(en)_2HgI_4$. [c] By precipitation.

(ii) UV. For mercuridestannylation of tri-n-butylphenylstannane, the final reaction solutions gave UV spectra which were identical with those synthetic solutions made up of equimolar amounts of phenylmercuric iodide and tri-n-butyliodostannane at the relevant concentration.

(iii) Quantitative product analyses were carried out as follows. 10^{-2} *M* mercuric iodide (50 ml) and 10^{-2} *M* R_3SnPh (50 ml) were mixed and allowed to react at 40.0°C for several hours, during which period colourless crystals appeared. The solution was then poured into 100 ml of water containing 3 g of potassium iodide, resulting in the formation of a white precipitate of PhHgI (identified by its m.p. and infrared spectrum) which was filtered off, dried and weighed. Inorganic mercury(II) iodide remaining in the filtrate was determined by precipitation as the complex $Cu(en_3HgI_4)$ [27] (en = ethylenediamine). The results appear in Table 5.

Kinetic measurements

All kinetic measurements were made at fixed wavelength using a Pye Unicam SP 8000 Spectrometer, thermostatted to a temperature of ±0.1°C by means of a Haake circulating water bath, and equipped with a Pye Unicam AR 25 linear slave chart recorder.

Runs were followed by monitoring the change in absorbance of the complex $[R_3Sn^+][HgI_3^-]$ as a function of time, using a wavelength of 302 nm. Concentrations in the range 1×10^{-4} to 3.5×10^{-4} *M* in HgI_2 were employed.

Calculations of the second-order rate constants k_2 for step (1) were based on the assumption that the equilibrium constant K for formation of the $[R_2Sn^+][HgX_3^-]$ complex is much greater than unity, using data from the first 30% of reaction. The kinetic equation used was

$$V = k_2(a-x)(b-2x)$$

where a and b are the initial concentrations of organotin compound and HgI_2, respectively. The integrated rate equation for the case $a = b$ is

$$k_2 t = \frac{1}{a} \times \ln \frac{1}{2}\left(\frac{2D_\infty - D_t - D_0}{D_\infty - D_t}\right) \tag{18}$$

in terms of the measured absorbance (D) at $t = 0$, t, and infinity. Values of k_2 thus calculated showed standard deviations of less than 6%. Mean rate constants were reproducible to with ±3% from run to run. Rate constants at 3 or more intial reactant concentrations were usually in agreement to within ±5%.

Values of the second-order rate constant k_2' for the slow step in the reaction of mercury(II) iodide with tri-n-butylphenylstannane were obtained in two ways, both employing pseudo-first order conditions, with the organotin compounds in excess.

(i) Runs were set up to simulate 50% reaction in the case where $[\mathrm{Bu^n_3SnPh}]_0 = [\mathrm{HgI_2}]_0$, i.e. reaction mixtures contained equimolar amounts of tri-n-butylphenylstannane, tri-n-butyliodostannane, $\mathrm{HgI_2}$ and phenylmercuric iodide, all at half the initial concentration of $\mathrm{PhSnBu^n_3}$ (or $\mathrm{HgI_2}$) in runs used to calculate k_2.

Under these conditions, $\mathrm{HgI_2}$ and $\mathrm{Bu^n_3SnI}$ react to form the complex $[\mathrm{Bu^n_3Sn^+}][\mathrm{HgI_3^-}]$, resulting in a low concentration of free $\mathrm{HgI_2}$, hence pseudo-first-order kinetic equations were used for calculating k_2'. Values of k_2' thus determined were found to be identical to those obtained from runs at twice the initial concentration, with $a = b$.

Good pseudo-first order plots of $\ln\{(D_0 - D_\infty)/(D_t - D_\infty)\}$ against time were obtained under these conditions, and the standard deviation of the derived rate constant k_2' was found to be less than 10%.

(ii) The second-order rate constants k_2' were also obtained from runs used to measure k_2. As the reaction approaches 50% reaction, the absorbance becomes constant. Subsequently, the absorbance begins to decrease, as the complex

TABLE 6

VALUES OF k_2 (M^{-1} s^{-1}) FOR THE CLEAVAGE OF $\mathrm{PhSnBu^n_3}$ BY $\mathrm{HgI_2}$ (2.5×10^{-4} M in each) IN METHANOL AT 14.5°C

t (s)	D_t	$D_\infty - D_t$	$2D_\infty - D_t - D_0$	$\ln\frac{1}{2}\left\{\frac{2D_\infty - D_0 - D_t}{D_\infty - D_t}\right\}$ [a]	k_2
0	0.071	0.876	1.750	0.000	–
10	0.100	0.846	1.721	0.018	7.0
20	0.126	0.820	1.695	0.034	6.7
30	0.148	0.798	1.673	0.048	6.4
40	0.170	0.776	1.651	0.062	6.3
50	0.194	0.752	1.627	0.079	6.3
60	0.216	0.730	1.605	0.095	6.4
70	0.236	0.710	1.585	0.111	6.3
80	0.256	0.690	1.565	0.126	6.3
90	0.276	0.670	1.545	0.143	6.4
100	0.295	0.650	1.525	0.160	6.4
111	0.312	0.634	1.509	0.175	6.4
120	0.334	0.612	1.487	0.195	6.5
130	0.352	0.594	1.469	0.213	6.6
140	0.366	0.580	1.455	0.227	6.5
150	0.382	0.564	1.439	0.244	6.5
160	0.396	0.550	1.425	0.260	6.5
170	0.412	0.534	1.409	0.278	6.5
180	0.426	0.520	1.395	0.294	6.5
190	0.440	0.506	1.381	0.312	6.6
200	0.454	0.492	1.367	0.329	6.6
∞	0.946				avg. 6.5±0.1

[a] A plot of $\ln\frac{1}{2}\left\{\frac{2D_\infty - D_0 - D_t}{D_\infty - D_t}\right\}$ vs. t gives a straight line with zero intercept and slope 1.64×10^{-3} s^{-1}, leading to a value for k_2 of 6.6 M^{-1} s^{-1}. Regression analysis on all 21 points gives a value of $r = 0.999$. The degree of freedom $\psi = 5\%$.

TABLE 7

VALUES OF k_2' (M^{-1} s^{-1}) FOR THE REACTION OF PhSnBu$^n_3$ (1.0×10^{-4} M) WITH [Bu$^n_3$Sn$^+$][HgI$_3^-$] IN METHANOL AT 23.7°C [a]

t (min)	D_t	$D_t - D_\infty$	$\ln\{D_0 - D_\infty / D_t - D_\infty\}$	k_2'
0	0.968	0.756	0.000	–
30	0.862	0.650	0.151	0.87
60	0.764	0.552	0.314	0.87
90	0.681	0.469	0.477	0.88
120	0.611	0.399	0.640	0.89
150	0.551	0.339	0.803	0.89
180	0.500	0.288	0.966	0.89
210	0.457	0.245	1.128	0.90
240	0.420	0.208	1.291	0.90
270	0.389	0.177	1.454	0.90
300	0.365	0.153	1.617	0.90
330	0.339	0.127	1.780	0.90
360	0.320	0.108	1.943	0.90
390	0.304	0.092	2.105	0.90
420	0.290	0.078	2.268	0.90
450	0.277	0.065	2.431	0.90
480	0.268	0.056	2.594	0.90
∞	0.212			avg. 0.89±.02

[a] Linear correlation coefficient $r = 0.99991$ (17 points). Degree of freedom $\psi = 1\%$.

[R$_3$Sn$^+$][HgI$_3^-$] is removed via (3).Thus k_2' is calculated from the decay of [Bu$^n_3$Sn$^+$][HgI$_3^-$] in this slow step. Values of k_2' calculated by either method were identical to within ±5%. Some runs were carried out with rigorously degassed solutions, but no appreciable variation in rates was observed. In addition, no induction periods were observed with any of the kinetic runs. Typical data appear in Tables 6 and 7.

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