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# Transmethylation Reactions of Sodium Trimethylsilylpropionate and Sodium 2,2-Dimethyl-2-silapentane-5-sulfonate with Hg(II) Species

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## Abstract

The effects of temperature, pCl and concentration on the rate and extent of silicon carbon bond cleavage by mercury(II) species were studied by $^1H$ NMR. Transmethylation reactions were found to be first order with respect to each reactant and second order overall. The rate of reaction is strongly dependent upon the nature of the mercury(II) electrophile. A mechanism consistent with the kinetic data is proposed.

## Introduction

A variety of reports of metathetical reactions between organosilicon compounds and metal or metalloid electrophiles fall under the general reaction scheme described in the following equation:

$$R_4Si + MCl_n \longrightarrow R_3SiCl + RMCl_{n-1}$$

where M = Hg(II), Fe(III), Al(III), Ga(III), Bi(III) or Sb(V), and R = alkyl or aryl [1–5].

The relatively small amount of work that has been done with electrophilic reagents in the +2 oxidation state has been with silanes of the general type R–Z–$Si(CH_3)_3$ where R = hydrogen or alkyl and Z = vinyl, ethynyl or phenyl [6–8]. The only work of this type done in aqueous media is that of DeSimone [9], who noted in a study of the reactions of methylcobalamin that the water-soluble NMR standards sodium trimethylsilylpropionate (TSP) and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) were able to transfer in aqueous solutions one or more of their methyl groups to inorganic salts of mercury(II).

The principal goal of this investigation was to delineate the chemical and physical factors that influence the cleavage of a silicon–carbon bond by mercury(II) species in aqueous solutions. This reaction is important both for its general theoretical interest and also for its possible environmental significance [10–13].

Specifically, the intention of this investigation was to study the effects of intensive variables such as temperature, pCl, concentration, and ionic strength on the rate and extent of silicon carbon bond cleavage by mercury(II), and to develop a reaction model consistent with the kinetic data.

## Experimental

### *Nuclear Magnetic Resonance*

All $^1H$ NMR data were obtained on a Varian XL-100 NMR spectrometer. The CW and pulsed FT-NMR $^1H$ spectra were run in $d_2$-water; 5 mm NMR tubes were used. Data collection and processing were performed on a Model 620/L–100 Varian Data Machine. The temperature of the probe was held constant to within ±0.3 °C by the use of a Varian variable temperature controller.

### *Kinetic Studies*

In the kinetic studies, the longitudinal relaxation times ($T_1$) were determined using the inversion recovery method [14]. The pulse delays were set equal to $5T_1$ when a full 90° pulse was used. Normally a sufficient signal to noise ratio for reactant concentrations of 0.025 M was achieved after twenty-five transients. The reactant solutions were pipetted into a 5 mm NMR tube and the kinetic program was initiated. Products were identified by comparison of chemical shifts and coupling constants with authentic compounds. The time from the beginning up to the mid-point of each spectrum was defined as the total elapsed time.

More detailed descriptions of experimental procedures can be found in ref. 15.

## Results and Discussion

The reactions between $HgCl_2$ and sodium $d_4$-trimethylsilylpropionate (TSP) were designed to

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TABLE I. Observed Second-order Rate Constants for TSP and $HgCl_2$ at Several Temperatures in $D_2O$[a,b]

| Temperature (°C) | $K_{obs}$ Standard deviation ($l\ mol^{-1}\ s^{-1} \times 10^3$) |
|---|---|
| 30.0 | 1.48 ± 0.09 |
| 35.0 | 2.52 ± 0.13 |
| 40.0 | 4.29 ± 0.18 |
| 45.0 | 8.44 ± 0.21 |

[a] Initial concentration of TSP and $HgCl_2$ = 0.025 mol/l; the ionic strength = 0.100. [b] Nominally observed for 30% extent of reaction.

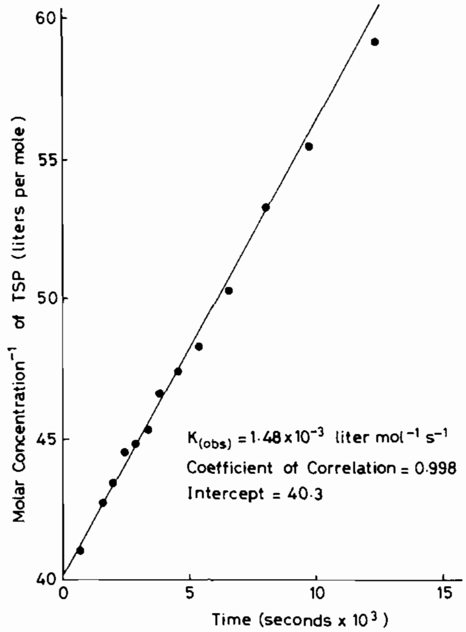


Fig. 1. The change in $[TSP]^{-1}$ with time at 30.0 °C.

determine the order of this reaction and the effect of temperature upon the observed rate constant. The changes in rate constant with temperature are reported in Table I, and the changes in concentration of TSP with time (the kinetic results) are given in Fig. 1. The initial concentrations of the reactants were held constant to minimize changes in their activities. The observed kinetics follow a simple second-order rate law, and the rate constants were found to increase with increasing temperature. A plot of the $\ln(K_{obs}/T)$ *versus* temperature is linear over the temperature range studied, as is shown in Fig. 2. The thermodynamic data listed in Table II were obtained following the procedures developed in the theory of absolute reaction rates [16]. The free energy of activation $\Delta G^{\ddagger}$ for the reaction of TSP with $HgCl_2$ (21.7 kcal $mol^{-1}$) is of similar magnitude but slightly greater than $\Delta G^{\ddagger}$ for the reaction of $(CH_3)_3SnCl$ and $HgCl_2$ or $TlCl_3$, which are 20.5 and 20.7 kcal $mol^{-1}$, respectively.

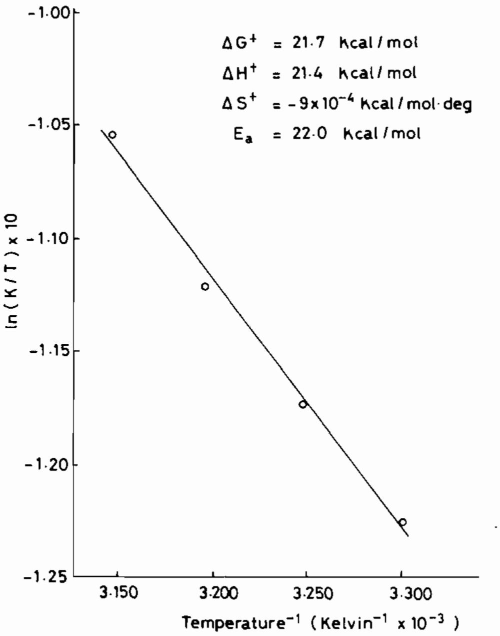


Fig. 2. Dependence of biomolecular rate constant on temperature for TSP and $HgCl_2$ transmethylation reaction.

The linearity of the rate data plotted as 1/[TSP] *versus* time indicates that, at least initially, the reaction is second-order, but it does not indicate the individual orders of $HgCl_2$ and TSP. The latter were determined by varying the relative concentrations of TSP and $HgCl_2$ and analyzing the data by applying the following rate equation:

$$K_{2(obs)}t = \frac{1}{(A - B)} \ln \frac{B(A - X)}{A(B - X)} \qquad (1)$$

TABLE II. Comparison of Activation Parameters for Transmethylation Reactions of Silicon and Tin Compounds in $D_2O$

| Reaction | $E_a$ (kcal/mol) | $\Delta G^{\ddagger}$ (kcal/mol) | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta S^{\ddagger}$ (kcal/mol deg) |
|---|---|---|---|---|
| TSP + $HgCl_2$[a] | 22.0 | 21.7 | 21.4 | −0.0009 |
| $(CH_3)_3Sn^+$ + $HgCl_2$[b] | 14.2 | 20.5 | 13.6 | −0.0230 |
| $(CH_3)_3Sn^+$ + $TlCl_3$[b] | 19.1 | 20.7 | 18.5 | −0.0074 |

[a] This work. [b] Ref. 23.

TABLE III. Observed Second-order Rate Constants[a] at Differing TSP/$HgCl_2$ Ratios in $D_2O$ at 30.0 °C.

| Ionic strength | TSP | $HgCl_2$ | TSP/$HgCl_2$ | $K_{2(obs)}$ (l $mol^{-1}$ $s^{-1}$ × $10^3$) |
|---|---|---|---|---|
| 0.100 | 0 0400 | 0 0200 | 2.00 | 1 88 |
| 0.100 | 0.0143 | 0.0286 | 0.500 | 1 73 |

[a] $r = 0.99$

TABLE IV. Influence of Counter-ions on the Observed Second-order Rate Constant for TSP and Hg(II) Transmethylation Reaction in $D_2O$

| Ionic strength | TSP (mol $l^{-1}$) | $HgCl_2$ (mol $l^{-1}$) | $Hg(NO_3)_2$ (mol $l^{-1}$) | NaCl (mol $l^{-1}$) | $NaNO_3$ (mol $l^{-1}$) | Cl/Hg | $T$ (°C) | $K_{2(obs)}$ × $10^3$ (l $mol^{-1}$ $s^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 0.100 | 0.0250 | 0.0250 | | | | 2.0 | 30 0 | 1 48 |
| 0 100 | 0.0125 | 0.0125 | | 0 0500 | | 6 0 | 30 3 | 2 20 |
| 0.100 | 0.0125 | 0.0125 | | | 0 0500 | 2.0 | 30.3 | 1.91 |
| 0 100 | 0.0250 | 0 0250 | | | | 2 0 | 45.0 | 8.44 |
| 0 100 | 0.0125 | 0.0125 | | 0.0500 | | 6.0 | 45.0 | 1 00 |
| 0.050 | 0.0125 | 0.0125 | | | | 2.0 | 30.0 | 1.73 |
| 0.050 | 0 0125 | 0.0063 | 0.0063 | | | 1.0 | 30.0 | 4 70[a] |

[a] Some precipitation of reactants upon mixing, the TSP–Hg(II) precipitate redissolves upon addition of chloride ion

TABLE V. Influence of Counter-ions on Observed Second-order Rate Constant for DSS and Hg(II) Transmethylation Reaction in $D_2O$

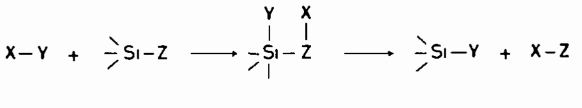
| Ionic strength | DSS (mol $l^{-1}$) | $HgCl_2$ (mol $l^{-1}$) | $Hg(ClO_4)_2$ (mol $l^{-1}$) | Cl/Hg | $T$ (°C) | $K_{2(obs)}$ × $10^3$ (l $mol^{-1}$ $s^{-1}$) |
|---|---|---|---|---|---|---|
| 0 100 | 0 0250 | 0 0250 | 0 0250 | 2.00 | 25 0 | 0.0025 |
| 0 100 | 0.0250 | 0.0094 | 0 0156 | 0 75 | 25 0 | 95 |
| 0 100 | 0.0250 | 0.0063 | 0.0188 | 0.50 | 25 0 | 200[a] |

[a] Slight precipitation of reactants upon mixing.

where A and B are initial reactant concentrations and X is the extent of reaction at time $t$. The results of the reaction of 0.400 M TSP with 0.0200 M $HgCl_2$ and the reaction of 0.0143 M TSP with 0.0286 M $HgCl_2$ are listed in Table III. The data were linear ($r = 0.99$) over 25% extent of reaction in each case. Thus, initially the reaction of TSP with $HgCl_2$ is first-order in TSP, first-order in $HgCl_2$, and second-order overall.

With the thermodynamic and empirical framework for the reaction of $HgCl_2$ with TSP established, attention was directed toward determining the mechanism of this reaction. Table IV is a tabulation of the results of reactions between TSP and Hg(II) with counter-ions of varying nature and concentration. As noted in Table IV, a portion of the TSP precipitated from solution upon addition of an equimolar $HgCl(NO_3)$ solution. In order to determine the effect of reducing the Cl/Hg ratio below two, the reaction of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) with Hg(II) was also studied and the results are presented in Table V.

It is proposed that the reaction of the silanes TSP and DSS with Hg(II) proceeds via a four-centered cyclic transition state [20] in which the poor leaving group is electrophilically abstracted by X with retention of configuration



$$X{-}Y + {>}Si{-}Z \longrightarrow \overset{Y\quad X}{{-}Si{-}Z} \longrightarrow {>}Si{-}Y + X{-}Z$$

A methide anion is a very poor leaving group and requires electrophilic assistance to facilitate its substitution. Thus, as the electrophilicity of the mercuric ion is increased, the rate of reaction should increase. This hypothesis is substantiated by the data presented in Table V. As the Cl/Hg ratio is decreased from 2 to 0.5, the observed second-order rate constant for the reaction of Hg(II) with DSS increases by five orders of magnitude. The rate of the DSS transmethylation reaction is clearly a very sensitive probe of the electrophilicity of Hg(II) under these reactions. It may be seen from Table IV that the reaction of TSP with Hg(II) also follows this trend when $Cl/Hg < 2$. This trend toward a slower reaction rate was not seen, however, at $Cl/Hg > 2$. Somewhat surprisingly, the observed second-order rate constant for the transmethylation reaction between TSP and Hg(II) remains nearly constant as the Cl/Hg ratio is increased from two to six, as shown in Table IV. This may be attributed to the fact that one would not expect a large change (~a factor of two) in the concentration of $HgCl_2$ between these two systems, since the tendency for mercury to increase its coordination from two to three is comparatively small [21]. Furthermore, the work of Jewett [22] has shown that the relative rates of reaction for $HgCl_2^{\circ}$ and $HgCl_3^-$ with a neutral trimethyltin(IV) species differ only by a factor of 1.12 with $HgCl_3^-$ the more reactive species. Thus, the chemistries of tin and silicon appear to resemble each other quite closely in systems in which the ratio of chloride ion to mercury(II) concentration is equal to or exceeds the stoichiometric amount. One may speculate that the decrease in electrophilicity of mercury in $HgCl_3^-$ is offset by the reduction in the strength of the individual Hg–Cl bonds, with the result that the energetics of the transition state, in which a Hg–C bond is being formed concurrent with the breaking of the Hg–Cl bond, are fortuitously similar to that for $HgCl_2$.

Implicit in these discussions of reaction mechanism is the formation of a silicon–halogen bond in aqueous solution. The strongest evidence for its existence is the kinetic behavior of DSS with Hg(II). As shown in Fig. 3, the reaction of DSS with $HgCl_{0.75}(ClO_4)_{1.25}$ is nearly linear over the entire course of the reaction. If chloride were not being sequestered after each successful reaction of DSS with Hg(II), then the Cl/Hg ratio would necessarily increase and thus the rate constant of the transmethylation reaction should decrease. The methylmercury(II) cation produced can form a complex with chloride ion [23]:

$$\log \frac{[CH_3HgCl]}{[CH_3Hg^+][Cl^-]} = 5.25 \tag{2}$$

However, the mercuric ion and the monochloromercurate ion both bind chloride ion more strongly [21].

$$\log \frac{[HgCl^+]}{[Hg^{2+}][Cl^-]} = 6.72 \tag{3}$$

$$\log \frac{[HgCl_2]}{[HgCl^+][Cl^-]} = 6.51 \tag{4}$$

Therefore, pCl buffering by methylmercury(II) does not occur to a significant extent until the later stages of the reaction. For example, at 70% reaction completion the total concentrations of Hg(II), $CH_3Hg(II)$ and $Cl^-$ are respectively, $7.50 \times 10^{-3}$ mol $l^{-1}$, $1.75 \times 10^{-2}$ mol $l^{-1}$, and $1.88 \times 10^{-2}$ mol $l^{-1}$. Substitution of these values into the above equilibrium expressions affords the value $7.49 \times 10^{-3}$ mol $l^{-1}$ for $[HgCl_2^{\circ}]$. Essentially all the Hg(II) remaining is in the form of $HgCl_2^{\circ}$ and (ignoring possible mercury(II)–sulfonate complexation) one would expect the observed rate constant to have decreased five orders of magnitude to a value similar to that observed for DSS and $HgCl_2$ [24]. Since this is not observed, the implication is that a Si–Cl bond *in situ* is formed which is stable to hydrolysis over the course of reaction.

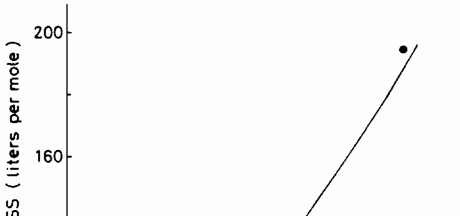


Fig. 3. The change in $[DSS]^{-1}$ with time at 25.0 °C; Cl/Hg = 0.75.

Figure 4 shows the deviation from second order kinetics that is observed at extents of reaction greater than ~30% in the TSP transmethylation reaction with $HgCl_2$. The cause of this deviation is primarily due to the competitive reaction of demethylated TSP (DSP) with $HgCl_2$. McMillan [25] has devised the following simple formula for the determination of the ratios of the bimolecular rate constants for two competing reactions.

$$K \ln \beta = \ln[\beta + (1 - K)\gamma] \tag{5}$$

where $K$ is the ratio of second order rate constants, $\beta$ = TSP concentration at time $t$ divided by TSP concentration at time 0, and $\gamma$ = DSP concentration at time $t$ divided by TSP concentration at time 0. Substitution for the observed $\beta$ and $\gamma$ at 60% extent

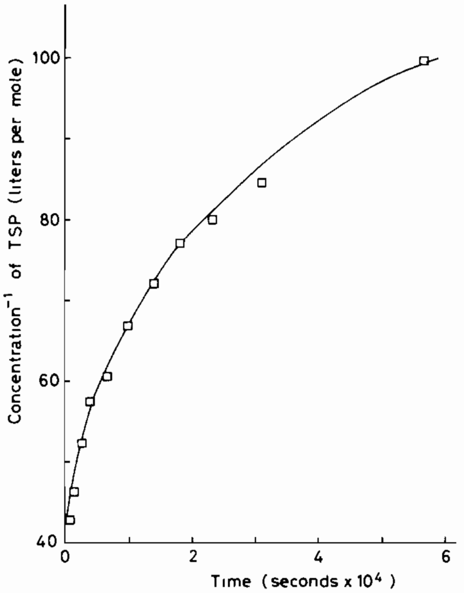


Fig. 4 The change in $[TSP]^{-1}$ with time at 40 0 °C.

of reaction results in a value of $K = 0.214$. Thus the observed second order rate constant for DSP and Hg(II) under these reaction conditions is calculated to be $9.18 \times 10^{-4}$ l $mol^{-1}$ $s^{-1}$. The lower reactivity of DSP is in accord with the deactivating behavior of chlorine (or oxygen) observed in other systems of electrophilic silicon–carbon bond cleavage.

A comment on ionic strength and activity coefficients is in order. The ionic strengths reported for these reactions were calculated as the summation of the products of the molar concentrations and the square of their formal charges of all ionic species. Complexation between oppositely charged ions (*i e.*, $Hg^{2+}$ and $Cl^-$) was ignored Solutions of identical ionic strength may not result in identical activity coefficients for all reactive species [26]. Furthermore, as the reaction proceeds, the calculated ionic strength drops as $Hg^{2+}$ is converted to the singly charged cation $CH_3Hg^+$. The activity coefficients of the reactants, therefore, may also change with extent of reaction. Finally, systematic studies designed to determine the effect of ionic strength on the observed second order rate constant are hampered by the fact TSP and DSS are salted out of solution at ionic strengths greater than ~0.2.

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